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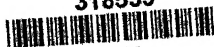
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# JOURNAL OF THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
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## PART I.

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### Organic Chemistry.

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**Fractionation of Crude Petroleum by Capillary Diffusion.** JOSEPH E. GILPIN and MARSHALL P. CRAM (*Amer. Chem. J.*, 1908, 40, 495—537).—It was observed by Day that when black vaselin is filtered through warm fuller's earth, the first product is liquid, whilst the succeeding portions become more and more viscous. This observation led to the discovery that a fractionation of crude petroleum can be effected in this way.

In the present investigation, tin tubes,  $5\frac{1}{2}$  feet long, packed with fuller's earth have been employed, the lower ends of which were immersed in the petroleum. It has been found that a fractionation of the oil takes place, the fractions rising to the top of the tube being of lower sp. gr. than those at the bottom. The paraffin hydrocarbons collect in the former fractions, and the unsaturated hydrocarbons in the latter. When water is added in successive quantities to fuller's earth which contains petroleum, the oil which is first displaced differs in sp. gr. from that which is displaced later. The whole of the oil cannot be displaced with water; about one-third remains in the fuller's earth.

E. G.

**Method of Production of Olefines by Decomposition of Esters.** ALBERT COLSON (*Compt. rend.*, 1908, 147, 1054—1059).—The author finds that the classical method for the preparation of ethylene is a particular case of a general reaction, since the esters of

organic or mineral acids decompose, at a sufficiently high temperature, into the corresponding acid and an olefine. Thus ethyl benzoate is unaltered when heated in sealed tubes at  $300^{\circ}$ ; at  $305\text{--}310^{\circ}$ , however, decomposition takes place, with formation of benzoic acid and ethylene. The action is most rapid at  $330^{\circ}$ ; after being heated for six hours at this temperature, the ester gave ten times its volume of hydrocarbon. Under the same conditions, amyl benzoate gave amylene. The yield of hydrocarbon is limited by the pressure of the gas, since, on allowing this to escape, a further quantity is obtained when the tube is re-heated. The benzoic acid has no influence on the reaction, which appears to be an irreversible one.

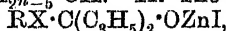
Ethyl stearate undergoes partial decomposition when distilled at  $224^{\circ}$ , but resists a temperature of  $300^{\circ}$  in the sealed tube; at  $315^{\circ}$  it furnishes stearic acid and ethylene. W. O. W.

**Dehydration of Commercial Methyl Alcohol.** JOSEPH GYR (*Ber.*, 1908, 41, 4322—4327. Compare Klason and Norlin, *Abst.*, 1906, i, 921).—The author prepares pure methyl alcohol from the acetone-free alcohol by first heating for some time with freshly burnt lime, then the alcohol is left in contact with ignited potassium carbonate for several weeks, and finally distilled several times over metallic calcium. For the first distillation, 10 grams of shavings per litre of methyl alcohol are used, the later distillations requiring less. As the calcium only reacts slightly in the cold, the temperature is raised, and the reaction proceeds, but care must be taken that alcohol does not distil over at this stage. When the bulk of the calcium has been acted on, the alcohol is distilled, the first fraction, which has a disagreeable odour, being collected separately. When all the water has been removed, the calcium reacts energetically with methyl alcohol if the temperature be not under control, so that only small quantities of the metal are required for the final distillation. The distillation over calcium is continued until the initial esterification constant of phenylacetic acid reaches the value 3.556. In one experiment, Kahlbaum's methyl alcohol from methyl oxalate had  $k = 0.465$ ; after one distillation over lime and potassium carbonate, 2.094; after a first distillation over calcium, 3.032; after a second, 3.279; after the third, 3.556. Magnesium amalgam is not a suitable agent for drying methyl alcohol.

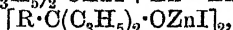
Pure methyl alcohol has  $D_{15}^{20} 0.79647$  and b. p.  $64.56^{\circ}/760$  mm. (compare Klason and Norlin, *loc. cit.*). 0.0524 volume % of water lowers the esterification constant of phenylacetic acid to 3.326, and 0.1254% to 2.976, so that the determination of this constant is even a better criterion than the density for determining whether the alcohol is pure. W. R.

**Synthesis of Alcohols of the Series  $C_nH_{2n-5}OH$ .** ALEXANDER N. REFORMATSKY (*Ber.*, 1908, 41, 4083—4102; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1182—1238).—The action of allyl iodide and zinc on esters of halogen derivatives of carboxylic acids in ethereal solution proceeds in three different directions, represented by the following equations, in which  $R$  represents a bivalent hydrocarbon radicle,  $R'$  a univalent

hydrocarbon radicle, and  $X$ , a halogen atom: I. (a)  $RX \cdot COOR' + ZnI \cdot C_3H_5 = RX \cdot C(OZnI)(C_3H_5) \cdot OR'$ ; (b)  $RX \cdot C(OZnI)(C_3H_5) \cdot OR' + ZnI \cdot C_3H_5 = RX \cdot C(C_3H_5)_2 \cdot OZnI + ZnI \cdot OR'$ ; (c)  $RX \cdot C(C_3H_5)_2 \cdot OZnI + ZnI \cdot C_3H_5 = C_3H_5 \cdot R \cdot C(C_3H_5)_2 \cdot OZnI + ZnIX$ ; (d)  $C_3H_5 \cdot R \cdot C(C_3H_5)_2 \cdot OZnI + H_2O = C_3H_5 \cdot R \cdot C(C_3H_5)_2 \cdot OH + ZnI \cdot OH$ , the product obtained being an unsaturated, monohydric alcohol having the general formula  $C_nH_{2n-5} \cdot OH$ . II. The compound,

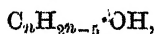


formed according to equation (b) above, reacts with the excess of zinc present, thus:  $2RX \cdot C(C_3H_5)_2 \cdot OZnI + Zn = ZnX_2 +$



the latter being then decomposed by water, giving the tetra-allylglycol,  $OH \cdot C(C_3H_5)_2 \cdot R \cdot R \cdot C(C_3H_5)_2 \cdot OH$ . III.  $RX \cdot C(C_3H_5)_2 \cdot OZnI + Zn + RX \cdot CO_2R' = ZnX_2 + CO_2R' \cdot R \cdot R \cdot C(C_3H_5)_2 \cdot OZnI$ , which, with water, yields the ester of a diallylhydroxy-acid,  $CO_2R' \cdot R \cdot R \cdot C(C_3H_5)_2 \cdot OH$ ; on hydrolysis, this ester yields either the free acid or the corresponding

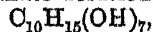
lactone,  $O < \begin{matrix} C(C_3H_5)_2 \cdot R \\ CO \end{matrix} \text{---} R$ . The proportion of the alcohol,



obtained diminishes, and that of the condensation products increases, as the molecular weight of the chloro-ester increases.

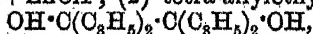
The alcohols,  $C_nH_{2n-5} \cdot OH$ , are colourless liquids with an odour resembling that of the terpenes, and are insoluble in water, but readily soluble in alcohols or ethers. They exhibit unexpected stability, for they do not oxidise appreciably in the air, although, when repeatedly distilled, they decompose to some extent, with formation of water. Their acetyl derivatives are obtained with difficulty, but the alcohols readily undergo bromination, which is, however, always accompanied by evolution of hydrogen bromide. They are readily oxidised by 1% potassium permanganate solution, yielding heptahydric alcohols. The boiling point and density of the alcohols rise as the molecular weight increases; the presence of an iso-radicle lowers the boiling point and also the yield of the alcohol.

*Triallylcarbinol*,  $OH \cdot C(C_3H_5)_3$ , prepared by the action of allyl iodide and zinc on ethyl chloro-formate, has b. p. 191—192°,  $D_0^{21}$  0.87829,  $D_4^{21}$  0.8781,  $n_D^{21}$  1.4680. Bromination yields the *hexabromide*,  $C_{10}H_{15}OBr_6$ , which loses hydrogen bromide, giving the *compound*,  $C_{10}H_{15}OBr_5$ . Oxidation with 1% permanganate solution yields the *heptitol*,



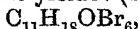
which could not be obtained pure, but yields a *hepta-acetyl* derivative,  $C_{10}H_{15}(OAc)_7$ , in the form of a dark brown syrup. Oxidation of triallylcarbinol with 3% permanganate solution yields oxalic and other acids. Attempts to prepare the methyl ether corresponding with the alcohol led to no definite results, as also did experiments made with the object of removing water from the alcohol and obtaining the corresponding hydrocarbon.

The triallylcarbinol, obtained as described above, is accompanied by: (1) crotonic acid, probably formed by isomeric change of vinylacetic acid, itself due to the reaction:  $CH_2 \cdot CH \cdot CH_2I + Zn + Cl \cdot CO_2Et = CH_2 \cdot CH \cdot CH_2 \cdot CO_2Et + ZnClI$ ; (2) tetra-allylethylene glycol,

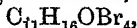


which is obtained as an odourless, yellow syrup, b. p.  $160^{\circ}/12$  mm., and is being investigated further.

*Diallylcrotonylcarbinol*,  $\text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CH}_2\cdot\text{C}(\text{C}_3\text{H}_5)$ , prepared by the action of allyl iodide and zinc on ethyl bromo- or chloro-acetate, is a moderately viscous liquid, b. p.  $217^{\circ}$ ,  $D_4^{18}$  0.8823,  $D_4^{18}$  0.88218,  $n_D^{18}$  1.474. On bromination, it yields: (1) the *hexabromide*,



which gradually loses hydrogen bromide, giving  $\text{C}_{11}\text{H}_{17}\text{OBr}_5$ ,

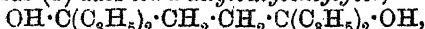


and lower brominated products; and (2) the *tetrabromide*,



which is a stable compound. Oxidation of the alcohol with 1% permanganate solution yields the *heptitol*,  $\text{C}_{11}\text{H}_{17}(\text{OH})_7$ , which was not obtained pure, and which, on acetylation, loses water and gives an *acetyl* derivative having the composition  $\text{C}_{11}\text{H}_{17}\text{O}(\text{OAc})_5$ . Attempts to remove  $\text{H}_2\text{O}$  from the alcohol,  $\text{C}_{11}\text{H}_{18}\text{O}$ , and thus obtain the hydrocarbon,  $\text{C}_{11}\text{H}_{16}$ , gave no definite result.

The action of allyl iodide and zinc on ethyl bromo- or chloro-acetate also yields (1) *ααδδ-tetra-allylbutyleneglycol*,

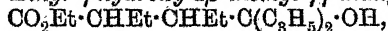


b. p.  $200-213^{\circ}/10$  mm.; which is being investigated, and (2) probably the ester,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{OH}$ .

*Diallyl-α-allylethylcarbinol*,  $\text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CHMe}\cdot\text{C}_3\text{H}_5$ , prepared by the action of allyl iodide and zinc on ethyl α-bromopropionate, is a colourless oil, b. p.  $223-224^{\circ}$ ,  $D_4^{22}$  0.876193,  $D_4^{22}$  0.876024,  $n_D^{22}$  1.4692. On bromination, it yields the *hexabromide*,  $\text{C}_{12}\text{H}_{20}\text{OBr}_6$ , which loses hydrogen bromide, at first rapidly, giving the compound  $\text{C}_{12}\text{H}_{19}\text{OBr}_5$ , and subsequently more slowly. On oxidation with 1% permanganate solution, it gives the *heptitol*,  $\text{C}_{12}\text{H}_{19}(\text{OH})_7$ , the *hepta-acetyl* derivative of which,  $\text{C}_{12}\text{H}_{19}(\text{OAc})_7$ , was prepared. The action of allyl iodide and zinc on ethyl α-bromopropionate also yields the *lactone* of γ-hydroxy-

*αβ-dimethyl-γγ-diallylbutyric acid*,  $\begin{matrix} \text{CHMe}\cdot\text{C}(\text{C}_3\text{H}_5)_2 \\ \text{CHMe}\text{---CO} \end{matrix} > \text{O}$ , b. p.  $155-160^{\circ}/15$  mm.

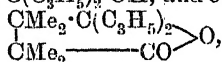
*Diallyl-α-allylpropylcarbinol*,  $\text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CHEt}\cdot\text{C}_3\text{H}_5$ , prepared by the action of allyl iodide and zinc on ethyl α-bromobutyrate, is a colourless, oily liquid, b. p.  $235-236^{\circ}$ ,  $D_4^{19}$  0.88303,  $D_4^{19}$  0.8817,  $n_D^{19}$  1.471. On bromination, it yields the *bromide*,  $\text{C}_{13}\text{H}_{18}\text{OBr}_4$ , formed by the loss of  $2\text{HBr}$  from the hexabromide. Oxidation by means of 1% permanganate solution yields the *heptitol*,  $\text{C}_{13}\text{H}_{21}(\text{OH})_7$ , which, on acetylation, undergoes dehydration and gives the *acetyl* derivative,  $\text{C}_{13}\text{H}_{21}\text{O}(\text{OAc})_5$ . *Ethyl γ-hydroxy-αβ-diethyl-γγ-diallylbutyrate*,



has b. p.  $161-162^{\circ}$ .

*Diallyl-α-allylisopropylcarbinol*,  $\text{OH}\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{CMe}_2\cdot\text{C}_3\text{H}_5$ , prepared by the action of allyl iodide and zinc on ethyl α-bromoisobutyrate, is a colourless, oily liquid, b. p.  $235^{\circ}$ ,  $D_4^{19}$  0.8942,  $D_4^{19}$  0.8928,  $n_D^{19}$  1.4760. On bromination, it yields the *bromide*,  $\text{C}_{13}\text{H}_{21}\text{OBr}_5$ . Oxidation with 1% permanganate solution gives the *pentitol*,  $\text{C}_{13}\text{H}_{21}\text{O}(\text{OH})_5$ , the *penta-acetyl* derivative of which,  $\text{C}_{13}\text{H}_{21}\text{O}(\text{OAc})_5$ , was prepared. The action of allyl iodide and zinc on ethyl α-bromoisobutyrate also yields a

mixture of the ethyl ester of  $\gamma$ -hydroxy- $\alpha\alpha\beta\beta$ -tetramethyl- $\gamma\gamma$ -diallylbutyric acid,  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{C}(\text{C}_3\text{H}_5)_2\cdot\text{OH}$ , and of its lactone,



b. p. 195—196°/15 mm.

T. H. P.

**Methyl and Ethyl Esters of Thiophosphoric Acid.** P. PISTSCHIMUKA (*Ber.*, 1908, 41, 3854—3859).—Alcohols react with phosphorus thiochloride, forming acid chlorides of the type  $\text{PSCl}_2\cdot\text{OR}$ , which, when treated with sodium alkyl oxides, yield neutral esters of thiophosphoric acid. The latter substances readily form additive compounds with salts, which decompose when heated; thus the additive compound,  $\text{PS}(\text{OMe})_3\cdot 2\text{HgCl}_2$ , when heated, decomposes thus:  $\text{PS}(\text{OMe})_3\cdot 2\text{HgCl}_2 \rightarrow \text{PS}(\text{OMe})(\text{OHgCl})_2 + 2\text{MeCl}$ .

Methyl thiophosphate forms with sodium methoxide the salt,  $\text{PO}(\text{SNa})(\text{OMe})_2$ , which, when treated with silver nitrate, yields the salt,  $\text{PO}(\text{SAg})(\text{OMe})_2$ ; the latter substance may also be obtained by adding an alcoholic solution of silver nitrate to the methyl ester; it forms stellate groups of white needles, and must have the constitution given, since, when treated with methyl iodide, it does not yield methyl thiophosphate, but gives rise to an ester,  $\text{PO}(\text{SMe})(\text{OMe})_2$ , a liquid, b. p. 103°/12 mm.,  $D_4^{20}$  1.2685.

The following additive products were prepared:  $\text{PS}(\text{OMe})_3\cdot 2\text{HgCl}_2$ ;  $3\text{PS}(\text{OMe})_3\cdot 2\text{FeCl}_3$ ;  $\text{PO}(\text{SHgCl})(\text{OEt})_2\cdot \text{HgCl}_2$ ;  $\text{PS}(\text{OMe})(\text{OHgCl})_2$ ;  $\text{PS}(\text{OMe})(\text{OTlCl})_2$ , yellow scales;  $\text{PO}(\text{SAG})(\text{OEt})_2$ , white crystals, m. p. 82°; and  $\text{PO}(\text{SNa})(\text{OEt})_2$ .

Methyl thiophosphate,  $\text{PS}(\text{OMe})_3$ , is an oil with an odour somewhat like ozone, b. p. 82°/20 mm.,  $D_4^{20}$  1.2192.

The following acid chlorides were prepared:  $\text{PSCl}_2\cdot\text{OMe}$ , b. p. 70°/40 mm.,  $D_4^{20}$  1.4949;  $\text{PSCl}_2\cdot\text{OEt}$ , b. p. 68°/20 mm.,  $D_4^{20}$  1.3966;  $\text{PSCl}_2\cdot\text{OPr}^n$ , b. p. 84°/20 mm.,  $D_4^{20}$  1.3344;  $\text{PSCl}_2\cdot\text{OPr}^s$ , b. p. 91°/20 mm.,  $D_4^{20}$  1.2724; they are colourless liquids, and are not decomposed by alcohols or water.

W. H. G.

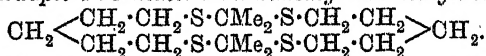
**Constitution of Phytin.** ERNST WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1908, 58, 118—121).—Phytin, the calcium magnesium salt of Posternak's anhydro-oxymethylenediphosphoric acid (*Abstr.*, 1903, ii, 680), is not appreciably affected by heating with saturated barium hydroxide solution at 180° or with 10% sodium hydroxide solution for one hundred hours, but when heated at 220—230° for twenty to twenty-four hours with 20% sodium hydroxide, it yields inositol and phosphoric acid. The compound is thus an inositolphosphoric acid. J. J. S.

**The Lability of Lecithin.** WOLFGANG HEUBNER (*Arch. exp. Path. Pharm.*, 1908, 59, 420—423).—The unstable nature of the lecithin molecule is shown by the fact that, after heating with alcohol, the platinum salt obtained is not pure choline platinichloride, but, in part, that of a base of lower molecular weight. The lecithin cadmium chloride also undergoes alteration in composition when recrystallised. Ovo-lecithin was employed.

W. D. H.

**Pentamethylene Mercaptans and Multi-membered Cyclic Mercaptols and Disulphones.** WILHELM AUTENRIETH and ALFRED GEYER (*Ber.*, 1908, 41, 4249—4256. Compare Abstr., 1899, i, 579, 580; 1902, i, 389).—*Pentamethylene mercaptan*,  $\text{SH}[\text{CH}_2]_5\text{SH}$ , obtained by the action of an alcoholic solution of potassium hydrogen sulphide on  $\alpha$ -dibromopentane (Braun, Abstr., 1904, i, 841), is a clear, colourless liquid, b. p. 108—109°/15 mm. or 123°/27 mm., and dissolves readily in organic solvents and in alkalis. The lead derivative,  $\text{C}_5\text{H}_{10}\text{S}_2\text{Pb}$ , forms a lemon-yellow, amorphous powder. The *dibenzoate*,  $\text{C}_5\text{H}_{10}(\text{S}\cdot\text{COPh})_2$ , crystallises from alcohol in slender needles, m. p. 45°. The ethers are readily obtained by the action of alkyl halides on the potassium salt, and when oxidised with permanganate yield the corresponding disulphones. *Pentamethylene- $\alpha$ -diethylsulphone*,  $\text{C}_5\text{H}_{10}(\text{SO}_2\text{Et})_2$ , crystallises from alcohol in glistening plates, m. p. 154°, and the corresponding *dibenzylsulphone*,  $\text{C}_5\text{H}_{10}(\text{SO}_2\cdot\text{C}_6\text{H}_5)_2$ , has m. p. 162—163°.

By the action of hydrogen chloride on a dry ethereal solution of acetone and pentamethylene mercaptan, a cyclic compound is formed, which crystallises from alcohol or acetone in plates with a pearly lustre. It has m. p. 117—118°, a molecular weight 352, and is probably *cycloduplo-1:3-dithio-2:2-dimethylhexamethylene*,



When oxidised with acidified 5% permanganate solution, it yields the corresponding *cyclo-1:3-disulphone*,  $\text{C}_{16}\text{H}_{32}\text{O}_8\text{S}_4$ , which crystallises from aqueous acetone in slender needles, m. p. 270°.

The *2:2-diethyl* derivative,  $\text{C}_{20}\text{H}_{40}\text{S}_4$ , obtained from diethyl ketone and pentamethylene mercaptan, crystallises from alcohol in needles, m. p. 113°, and yields a *disulphone*,  $\text{C}_{20}\text{H}_{20}\text{O}_8\text{S}_4$ , m. p. 260° (decomp.).

J. J. S.

**Constitution of Disulphoxides. II.** OSCAR HINSBERG (*Ber.*, 1908, 41, 4294—4297. Compare Abstr., 1908, i, 875).—The synthesis of ethyl disulphoxide from potassium ethanethiosulphonate and ethyl bromide would appear to be against the compound being symmetrical, but from Gutmann's results (Abstr., 1908, i, 972) the aryl thiosulphonates are probably of the constitution  $\text{R}\cdot\text{SO}\cdot\text{S}\cdot\text{OM}$ , and not  $\text{R}\cdot\text{SO}_2\cdot\text{SM}$ , and therefore the symmetrical formula for disulphoxides is strengthened. Further evidence in support of this conclusion is furnished by the easy reduction of  $\beta$ -naphthyl disulphoxide to disulphide by sulphurous acid in the presence of a small quantity of hydriodic acid; neither sulphinic acid nor mercaptan could be detected.

W. R.

**Total Asymmetric Synthesis.** FRANZ HENLE and HERMANN HAAKH (*Ber.*, 1908, 41, 4261—4264).—In previous attempts to obtain asymmetric syntheses by means of circularly polarised light, reactions have been employed which are not affected by light, for example, the addition of hydrogen to benzoylformic acid. The authors have investigated the elimination of carbon dioxide from certain carboxylic acids, a reaction which is influenced to a consider-

able extent by light, but asymmetric synthesis was not observable. The substances employed were  $\alpha$ -cyano- $\alpha$ -methylbutyric acid and dichloro- $s$ -dimethylsuccinic acid (Abstr., 1892, i, 142).

*Ethyl  $\alpha$ -cyano- $\alpha$ -methylbutyrate*,  $\text{CN}\cdot\text{CMeEt}\cdot\text{CO}_2\text{Et}$ , has b. p.  $198^\circ$ , and the corresponding acid,  $\text{CN}\cdot\text{CMeEt}\cdot\text{CO}_2\text{H}$ , obtained by hydrolysing the ester with 25% methyl alcoholic potash, has m. p.  $39^\circ$ .

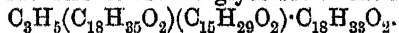
It is pointed out that it is not necessary that the light should be first plane polarised for this type of experiment. J. J. S.

**Solid Constituents of Japanese Train Oil.** H. OKADA (*Chem. Zeit.*, 1908, 32, 1199—1201).—Repeated extraction with ether and cooling the extract to  $-10^\circ$  gave a solid product, which was purified by fractional dissolution in ether-alcohol mixtures of various strengths. This treatment led to a more or less complete separation of a substance, m. p.  $34$ — $35^\circ$ , having a saponification number, an acid number, and an iodine value in very fair agreement with the mixed glyceride,  $\text{C}_5\text{H}_9(\text{C}_{17}\text{H}_{33}\text{O}_2)_2\cdot\text{C}_{18}\text{H}_{33}\text{O}_2$  (Holde, Abstr., 1901, i, 577).

When saponified, this substance gave a liquid fatty acid having a molecular weight and saponification value in agreement with oleic acid; also a white, crystalline compound, m. p.  $43$ — $47^\circ$ , which is possibly a mixture of stearic acid and *isocetic* acid ( $\text{C}_{18}\text{H}_{36}\text{O}_2 + \text{C}_{15}\text{H}_{30}\text{O}_2$ ).

This mixture, when dissolved in alcohol and cooled by ice, deposited a crystalline mass, m. p.  $56$ — $59^\circ$ , whilst from the mother liquor there was obtained a substance, m. p.  $44$ — $47^\circ$ . After fractionally precipitating these substances by adding magnesium acetate to the alcoholic solutions, each was obtained in an apparently pure state, m. p.  $57$ — $59^\circ$  and  $44$ — $47^\circ$  respectively.

From the evidence at present available, the conclusion is drawn that these substances are derived from a glyceride of the form



J. V. E.

**$\beta$ -Cinenic Acid.** HANS RUPE and H. ALTENBURG (*Ber.*, 1908, 41, 3952—3957).— $\beta$ -Cinenic acid, first obtained by heating  $\alpha$ -cinenic acid with dilute sulphuric acid, was held to be a stereoisomeride of the  $\alpha$ -acid (Abstr., 1901, i, 578), because the addition of hydrogen bromide gave with the two acids  $\epsilon$ -bromo- $\alpha$ -hydroxy- $\alpha$ -dimethylheptioic acid. As the yield from the  $\beta$ -acid was very poor, the subject has been reinvestigated.

A more convenient method of separating the  $\beta$ - from the  $\alpha$ -acid is by the action of hydrochloric acid on a methyl-alcoholic solution of the mixture. The  $\alpha$ -acid gives a chlorinated ester boiling  $30$ — $35^\circ$  higher than the methyl  $\beta$ -cinenate formed simultaneously, and the pure  $\beta$ -acid is obtained by hydrolysis of the methyl ester, b. p.  $127$ — $128^\circ/12$  mm.,  $n_D^{20}$  1.45083; *ethyl* ester, b. p.  $92$ — $93^\circ/12$  mm.; the *silver*, *lead*, *uranium*, and *copper* salts have also been prepared. The acid could not be obtained solid, nor does it react with hydroxylamine or semicarbazide.

It is now found that a good yield of the bromohydroxydimethylheptioic acid is obtained if the  $\beta$ -cinenic acid is heated with a

saturated solution of hydrobromic acid in a closed tube at 56° for two hours and then at the ordinary temperature for twenty-four hours. The stereoisomerism of the two acids is, therefore, proved. The  $\beta$ -acid is not converted into the  $\alpha$ -isomeride on treatment with acetyl chloride.

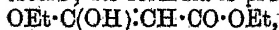
$\alpha$ -Cinenic acid crystallises with  $1\text{H}_2\text{O}$  from alcohol in triclinic plates [ $a:b:c = 0.7089:1:0.783$ ;  $\alpha = 106^\circ 23'$ ,  $\beta = 125^\circ 5'$ ,  $\gamma = 83^\circ 10'$ ], m. p. 76°. W. R.

**Decomposition of Ricinoleic Sulphuric Acid with Dilute Acids.** ADOLF GRÜN and H. WETTERKAMP (*Zeitsch. Farb.-Ind.*, 1908, 7, 375—376. Compare Grün, Abstr., 1907, i, 111).—The authors have investigated the products formed by treating ricinoleic sulphuric acid (sulphoricinoleic acid) with dilute acids, and find that their observations are in many cases not in agreement with those recently published by Wagner (*ibid.*, 284). When an aqueous solution of this ester is boiled, it does not liberate sulphur dioxide, but yields *ricinoleic ricinoleate*, thus:  $2\text{SO}_3\text{H}\cdot\text{O}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\cdot\text{C}_{17}\text{H}_{32}\cdot\text{CO}_2\text{H}$ . The latter is a yellowish-brown, viscid oil, forming a grey *silver* salt,  $\text{C}_{36}\text{H}_{65}\text{O}_5\text{Ag}$ . The sulphuric ester decomposes more rapidly when heated with dilute mineral acids, the product formed in this case being a neutral substance, probably the *lactide* of ricinoleic acid,  $\text{C}_{17}\text{H}_{32}\langle\begin{smallmatrix} \text{O}\cdot\text{CO} \\ \text{CO}\cdot\text{O} \end{smallmatrix}\rangle\text{C}_{17}\text{H}_{32}$ .

The isomeric ricinelaiddic sulphuric ester behaves in an analogous manner. W. H. G.

**The Claisen Condensation. III. Mechanism of the Reaction.** J. BISHOP TINGLE and ERNEST E. GORSLINE (*J. Amer. Chem. Soc.*, 1908, 30, 1874—1882).—A continuation of the work described in previous papers (Abstr., 1907, i, 498; 1908, i, 732). In order to ascertain whether in the formation of ethyl acetoacetate the sodium reacts directly with the ethyl acetate, or whether it reacts first with a trace of alcohol, experiments have been made with ethyl acetate carefully purified with phosphoric oxide and with calcium. The results show that the reaction with sodium takes place just as readily with this purified ester as with that prepared in the ordinary way. It has also been found that ethyl acetoacetate is readily formed from ethyl acetate and sodium in presence of ether. The velocity of the reaction is not reduced by the presence of the ether. It is evident, therefore, that ethyl acetate, entirely free from alcohol, reacts with sodium as readily as the ester containing a trace of alcohol.

Ethyl malonate, ethyl dimethylmalonate, and ethyl chloromalonate react with two, four, and one atoms of sodium respectively. These results indicate that ethyl malonate has a different structure from that of the other two esters; its formula is probably



whilst that of the dimethylmalonate is  $\text{CMe}_2(\text{CO}_2\text{Et})_2$ .

Experiments are described which show that the catalytic influence of ether and the tertiary bases in promoting the Claisen reaction is

general, and that the effect appears to depend on the velocity with which the particular ketone and ester react; if this is relatively small, the catalytic effect is considerable.

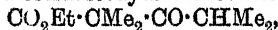
A condensation compound has been obtained from benzophenone and ethyl oxalate. The fact that this ketone, which does not contain a  $\text{CH}_3\cdot\text{CO}-$  or  $\text{RCH}_2\cdot\text{CO}-$  group, reacts in this manner shows that the Claisen-Nef hypothesis of the mechanism of the condensation is erroneous. Attempts have been made to condense acetaldehyde with various esters in presence of sodium, but without success.

Benzophenone combines with two atoms of sodium; by the action of water on the sodium derivative, benzhydrol and benzopinacolone are produced.

E. G.

**Action of Zinc on a Mixture of Esters of  $\alpha$ -Bromoisobutyric and Carbonic Acids.** M. L. SHDANOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1347—1367).—The action of zinc on a mixture of ethyl- $\alpha$ -bromoisobutyrate and ethyl carbonate yields, under all experimental conditions employed, ethyl dimethylmalonate,  $\text{CMe}_2(\text{CO}_2\text{Et})_2$ , b. p. 199.2—200.2°. Dimethylmalonic acid,  $\text{CMe}_2(\text{CO}_2\text{H})_2$ , crystallises from water in hexagonal, monoclinic prisms [ $\text{W. I. LYCHITSCHKY}$ :  $\beta = 104.8^\circ$ ], m. p. 185—186° (decomp.). The silver,  $\text{C}_5\text{H}_6\text{O}_4\text{Ag}_2$ , barium,  $\text{C}_5\text{H}_6\text{O}_4\text{Ba}$ , and zinc,  $\text{C}_5\text{H}_6\text{O}_4\text{Zn}\cdot 3\text{H}_2\text{O}$ , salts were prepared, the last crystallising from water in characteristic plates.

The ethyl dimethylmalonate formed was accompanied by small proportions of (1) ethyl tetramethylacetoacetate,



which, on hydrolysis with potassium hydroxide solution, yields alcohol and diisopropyl ketone; (2) ethyl trimethylglutarate.

When the proportions of the reacting substances are 1 atom of zinc, 2 mols. of ethyl  $\alpha$ -bromoisobutyrate, and 1 mol. of ethyl carbonate, the reaction also gives rise to ethyl tetramethylacetonedicarboxylate (compare Petrenko-Kritschenko, Pissarjewsky, and Herschkowitsch, *Abstr.*, 1896, i, 135).

It is found that the action of zinc on ethyl  $\alpha$ -bromoisobutyrate alone yields ethyl trimethylglutarate and ethyl tetramethylacetoacetate, so that in the formation of these products in the previous reaction the ethyl carbonate plays no part.\*

T. H. P.

**Ethyl Formylsuccinate and its Relationship with Aconic Acid.** WILHELM WISLICENUS, EMIL BÖKLEN, and FELIX REUTHE (*Annalen*, 1908, 363, 340—370. Compare *Abstr.*, 1900, i, 9).—It has been found possible to convert aconic acid into ethyl formylsuccinate to the extent of 80% of the theoretical yield by treating an alcoholic solution of the acid with hydrogen chloride, and thus to show the correctness of the view put forward previously, that ethyl formylsuccinate and aconic acid are respectively the ester and lactone of hydroxyitaconic acid (compare *Abstr.*, 1894, i, 127).

Ethyl formylsuccinate yields a copper salt,  $(\text{C}_9\text{H}_{15}\text{O}_5)_2\text{Cu}$ , which crystallises with 2Et·OH in glistening, green needles; the alcohol-free salt has m. p. 132—133°; the nickel salt,  $(\text{C}_9\text{H}_{15}\text{O}_5)_2\text{Ni}$ , forms tufts of

bright green needles, m. p. 219—220°. The ester combines with phenylcarbimide, forming an *additive* product,

$\text{NHP} \cdot \text{CO} \cdot \text{O} \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , glistening, colourless prisms, m. p. 103—104°, and yields a *benzoyl* derivative,  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH} \cdot \text{OBz}$ , long, colourless needles, m. p. 57—58°, b. p. 130—140°/24 mm.; the *p*-nitrobenzoyl derivative,  $\text{C}_{10}\text{H}_7\text{O}_5\text{N}$ , forms long, glistening needles, m. p. 104°.

An 80% yield of  $\beta$ -aldehydopropionic acid is obtained by heating the formylsuccinic ester with water under pressure at 120—130°; the phenylhydrazone phenylhydrazide of the aldehydo-acid has m. p. 188—189°: Perkin and Sprankling give m. p. 192° (Trans., 1899, 75, 16); the same compound is formed by the action of phenylhydrazine on aconic acid (compare Reitter and Bender, Abstr., 1905, i, 669). Ethyl formylsuccinate is converted by phenylhydrazine (1 mol.) into a substance which is probably *ethyl 1-phenyl-5-pyridazinone-4-carboxylate*,  $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{N} = \text{CH} \end{smallmatrix} \text{CH} \cdot \text{CO}_2\text{Et}$ , pale yellow leaflets, m. p. 111—112°, since the corresponding *acid*,  $\text{C}_{11}\text{H}_{10}\text{O}_3\text{N}_2$ , small, slightly yellow prisms, m. p. 178—179°, when oxidised by potassium permanganate, is converted into an *acid*,  $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{CH} \\ \text{N} = \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$  (?), obtained as a yellow powder, m. p. 181—182°; the *silver* salt,  $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2\text{Ag}$ , is a yellow powder.

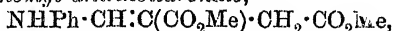
*Ethyl p-toluidino- $\gamma$ -itaconate*,  $\text{C}_8\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , is prepared by the action of *p*-toluidine on ethyl formylsuccinate; it forms white crystals, m. p. 115—116°, and gives off alcohol when heated above 150°.

Ethyl formylsuccinate is reduced by "active" aluminium to ethyl itamalatate, and is converted by phosphorus pentachloride into *ethyl chloroitaconate*,  $\text{CHCl} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , a colourless liquid with a pleasant, fruity odour, b. p. 125°/20 mm., which, when hydrolysed, yields a *chloroitaconic acid*,  $\text{C}_6\text{H}_5\text{O}_4\text{Cl}$ , obtained as small, colourless crystals, m. p. 150—151°, not identical with the chloroitaconic acid described by Swarts (*Jahresb.*, 1873, 584), since it is not decomposed when boiled with water; the two acids are possibly geometrical isomerides. The *methyl hydrogen* ester,  $\text{CHCl} : \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$  or  $\text{CHCl} : \text{C}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared by heating the acid just described with methyl alcohol in a closed tube at 130—140°, crystallises in colourless rhombohedra, m. p. 74—75°.

*Ethyl aconate*,  $\text{CO} \begin{smallmatrix} \text{O} \cdot \text{CH} \\ \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$ , obtained by the action of ethyl iodide on silver aconate, is a colourless, almost odourless oil, b. p. 144—145°/18 mm. Methyl formylsuccinate has b. p. 112—115°/12 mm. (compare von Rothenburg, Abstr., 1894, i, 302); it yields a *copper* salt,  $(\text{C}_7\text{H}_5\text{O}_5)_2\text{Cu} \cdot \text{H}_2\text{O}$ , which crystallises in green needles or leaflets, m. p. 133—135°; the *anhydrous* salt is greenish-yellow, and has m. p. 144—145°. The green salt when boiled with methyl alcohol is converted into a *basic methoxide*,

$\text{CO}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Me}) \cdot \text{CH} \cdot \text{O} \cdot \text{Cu} \cdot \text{OMe}$ , which crystallises in stellate groups of small, blue prisms, m. p. 193—194°.

Phenylhydrazine (1 mol.) and aniline convert methyl formylsuccinate into the substance,  $C_{12}H_{12}O_3N_3$ , yellow scales, m. p. 133—134°, and *methyl anilinoitaconate*,



tufts of microscopical needles, m. p. 91—93°, respectively.

Both ethyl and methyl formylsuccinate are converted by phenylhydrazine (2 mols.) into the substance,  $C_{17}H_{16}O_2N_4$ , m. p. 192—194° (decomp.), identical with that obtained by Reitter and Bender (*loc. cit.*) by the action of phenylhydrazine on methyl aconate. W. H. G.

**Acetonedicarboxylic Acid from Calcium Sucrate.** EDMUND O. VON LIPPMANN (*Ber.*, 1908, 41, 3981—3982. Compare Abstr., 1894, i, 105).—On opening a vessel in which calcium sucate had been kept for many years, a pronounced odour of acetone was observed, and the contents yielded a substance which was identified as acetonedicarboxylic acid by its m. p., 136° (decomp. into acetone and carbon dioxide), and by its conversion into diphenyltetrahydropyrone (compare Petrenko-Kretschenko, Abstr., 1898, i, 142). C. Š.

**State in Solution of the Tartrates of Aliphatic and Aromatic Amines as Revealed by their Rotatory Power.** JULES MINGUIN and HENRI WOHLGEMUTH (*Compt. rend.*, 1908, 147, 978—981. Compare Abstr., 1905, ii, 130; 1908, ii, 137).—The authors have measured the rotation of *M*/100 solutions of tartaric acid, and of its hydrogen and normal salts with propylamine, butylamine, diethylamine, and triethylamine, and of *M*/100 solutions of the normal salt containing an excess of the amine. The results verify Tschugaëff's rule (Abstr., 1898, i, 274, 495; 1899, ii, 3; Minguin and Bollemont, Abstr., 1903, i, 352), for all the hydrogen salts of the homologous series have the same rotatory power, as have also the normal salts, and show also that the normal salts are not dissociated in solution, since the rotation is not changed by the addition of excess of the amine.

Similar measurements made with the tartrates of the aromatic amines, aniline, *o*-, *m*-, and *p*-toluidines, methylaniline, dimethylaniline, and diethylaniline show that these amines do not form normal salts, and that the hydrogen salts are dissociated in solution.

The *hydrogen tartrates* of *aniline*, *o*-, *m*-, and *p*-*toluidines*, *methyl-aniline*, and  *$\alpha$ -naphthylamine* have m. p. 172°, 154°, 149°, 182°, 92°, and 172° respectively. M. A. W.

**Nitrogen Pentoxide as a Nitrating Agent.** G. E. GIBSON (*Proc. Roy. Soc. Edin.*, 1908, 28, 705—707).—Tartaric acid dinitrate is more advantageously prepared by substituting nitrogen pentoxide for the ordinary nitrating mixture of fuming nitric acid and concentrated sulphuric acid, whereby subsequent treatment of the product with water is no longer necessary.

Finely-powdered tartaric acid is mixed with slightly more nitrogen pentoxide than is indicated by the equation  $C_4H_4O_4(OH)_2 + 2N_2O_5 = C_4H_4O_4(NO_3)_2 + 2HNO_3$ , and is kept over solid sodium hydroxide in an evacuated desiccator until practically free from nitric acid. The dinitrate is separated from unchanged tartaric acid by extracting with

dry ether; the solvent is removed by evaporating below  $40^{\circ}$ , and finally by placing in a vacuum over concentrated sulphuric acid. Tartaric acid dinitrate prepared by this method is a white, crystalline powder, and is obtained in 81% of the theoretical yield.

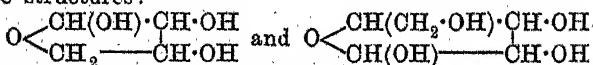
Details of a convenient method of preparing large quantities of nitrogen pentoxide from nitric acid and phosphoric anhydride are also given. J. V. E.

**Humic Substances of Coals.** OCTAVE BOUDOUARD (*Compt. rend.*, 1908, 147, 986—988).—The author has analysed the humic acid extracted by means of potassium hydroxide solution from seven varieties of coal, both before and after artificial oxidation. The results of the fourteen analyses show that the chemical constitutions of the humic substances thus obtained correspond with one or other of the formulæ: (1)  $C_{18}H_{14}O_6$  (Berthelot and André, *Abstr.*, 1891, 1089); (2)  $C_{18}H_{18}O_9$  (Malaguti), (3)  $C_{18}H_{14}O_9$ , (4)  $C_{18}H_{14}O_{11}$ , and that the effect of oxidising the coal is to diminish the carbon and increase the hydrogen and oxygen content of the humic substance yielded by the coal. M. A. W.

**Action of Ammonia on Methyl Ethyl Ketone.** WILHELM TRAUBE (*Arch. Pharm.*, 1908, 246, 666—675. Compare *Abstr.*, 1908, i, 362).—A reply to Thomae (*ibid.*, 762). T. A. H.

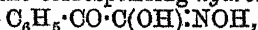
**Certain Aldehydic Compounds.** ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 360—366).—The authors have examined members of the following classes of compounds to ascertain whether they yield hydroxamic acids when treated with benzenesulphohydroxamic acid in presence of sodium hydroxide: (1) hydroxyaldehydes; (2) ketoaldehydes; (3) aldehydes containing nitrogen. The general results are that this reaction is not given by any of the aldehydes formed by the action of chloroform in presence of alkali or by aromatic hydroxyaldehydes, although the ethers corresponding with the latter do yield hydroxamic acids.

With the aliphatic hydroxyaldehydes, the presence of a hydroxyl group in the  $\gamma$ -position prevents the formation of a hydroxamic acid. Thus, whilst glycollaldehyde and glyceraldehyde yield hydroxamic acids, *d*-erythrose and *l*-arabinose do not; these sugars probably have the structures:



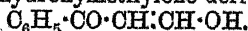
respectively, the latter configuration being also justified by the ease with which *l*-arabinose yields furfuraldehyde. Dextrose also does not yield a hydroxamic acid.

Phenylglyoxal gives the corresponding *hydroxamic acid*,



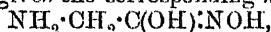
which separates from benzene in crystals, m. p.  $128^{\circ}$ .

Formylacetophenone does not yield a hydroxamic acid, and must be regarded as a hydroxymethylene derivative,



Neither levulinaldehyde nor *d*-glucosone yields a hydroxamic acid.

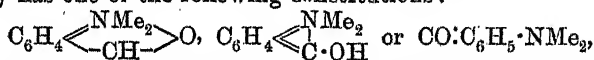
Aminoacetaldehyde gives the corresponding *hydroxamic acid*,



the *picrate* of which is obtained as a yellow precipitate, m. p. 108° (decomp.).

$\delta$ -Aminovaleraldehyde does not give a hydroxamic acid (compare Rimini, Abstr., 1901, i, 450).

*p*-Dimethylaminobenzaldehyde does not form a hydroxamic acid, and probably has one of the following constitutions :



the aromatic residue containing two double linkings as is the case with the quinones.

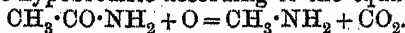
Pyrrole and indole aldehydes do not give hydroxamic acids (compare Abstr., 1907, i, 551). T. H. P.

**Colloidal Properties and Spontaneous Gelatination of Starch.** EUGÈNE FOUARD (*Compt. rend.*, 1908, 147, 931—933).—A pseudo-solution of starch at 15° gradually becomes opalescent and finally sets (compare Abstr., 1908, ii, 503). The molecular aggregates which are first coagulated are those with the largest rotatory power, as not only does the quantity of dissolved matter gradually diminish during several months, but also its specific rotatory power.

During extraction of starch grains and before coagulation begins, however, the larger molecular aggregates are slowly being broken down into smaller ones with low rotatory power. The hyperbolic equation representing the rate of coagulation is supposed to be the resultant of the two opposing changes. The heat transfer during these reversible changes must be very small, a supposition which is confirmed by the continuous circulation of starchy matter in living cells. R. J. C.

**Constitution of Sodium Cellulose.** O. MILLER (*Ber.*, 1908, 41, 4297—4304. Compare Abstr., 1908, i, 78).—Polemical. A reply to Viewig (Abstr., 1908, i, 857). W. R.

**Theory of the Preparation of Methylamine from Solutions of Acetylbroamide.** MAURICE FRANÇOIS (*Compt. rend.*, 1908, 147, 983—986 \*).—The author suggests that in the preparation of methylamine by Hofmann's method the bromine in the alkaline solution of bromine and acetamide is present as hypobromite and not as acetylbroamide, and the reaction consists in the oxidation of the acetamide by the hypobromite according to the equation :



In support of this theory, experiments are described which show (1) that the bromine in a solution of acetamide bromine and potassium hydroxide in molecular proportions can be estimated by the usual methods for determining hypobromous acid ; (2) that methylamine can be prepared by heating a solution containing potassium hypobromite and acetamide.

\* and *J. Pharm. Chim.*, 1909, 29, 5—9.

The bromine in a solution of acetamide and bromine in the presence of excess of calcium carbonate (Abstr., 1908, i, 956) is present partly as hypobromite and partly as free bromine, and the mixture has all the properties of Hofmann's acetylbromoamide.

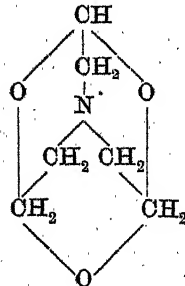
M. A. W.

**Additive Compounds of Selenium Dioxide.** F. CARNEVALI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 385—389).—When tetramethyl- or tetraethyl-ammonium chloride is added to a concentrated aqueous solution of a large excess of selenium dioxide containing hydrochloric acid, and the liquid evaporated to a syrup and allowed to cool in a vacuum over potassium hydroxide, an additive compound of selenium dioxide with tetramethyl- or tetraethyl-ammonium chloride of the composition  $\text{SeO}_2 \cdot 2\text{NMe}_4\text{Cl}$  or  $\text{SeO}_2 \cdot 2\text{NEt}_4\text{Cl}$  is deposited. Both these compounds form slightly yellow, deliquescent crystals, and are completely hydrolysed by water, to which they impart an acid reaction. Under the influence of light, they gradually decompose, giving small quantities of selenium (compare Muthmann and Schäfer, Abstr., 1893, ii, 318).

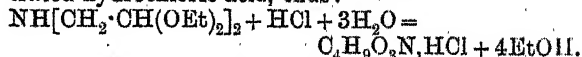
T. H. P.

**Diacetalylamine and Triacetalylamine.** LUDWIG WOLFF and RICHARD MARBURG (*Annalen*, 1908, 363, 169—220).—The authors have made a reinvestigation of diacetalylamine (diacetalamine, Wolff, Abstr., 1888, 809), with the object of ascertaining if the product obtained from it by the action of acids, which is probably iminodiacetaldehyde, can be converted into pyrazine by means of hydroxylamine. Diacetalylhydrazine was also examined with the same end in view, and the hitherto unknown triacetalylamine has also been prepared and examined. Di- and tri-acetalylamine, nitroso-acetalylamine, and diacetalylhydrazine are all much more sparingly soluble in hot water than in cold. The elimination of the acetal groups is best effected by means of concentrated hydrochloric acid.

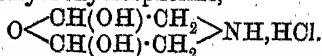
Triacetalylamine is decomposed by hot concentrated hydrochloric acid, thus:  $\text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_3 + 3\text{H}_2\text{O} = \text{C}_6\text{H}_5\text{O}_3\text{N} + 6\text{EtOH}$ , with the formation of a well-crystallised, monoacid, tertiary base to which is assigned the constitution (annexed) of a trimorpholine.



Diacetalylamine is decomposed by cold concentrated hydrochloric acid, thus:

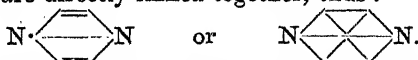
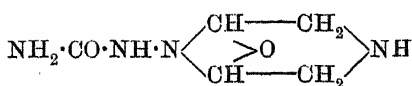


The salt formed (from which the base could not be prepared in a pure state) is regarded as the hydrochloride of dihydroxymorpholine,



This, when treated with hydrogen sulphide, yields dihydroxythiomorpholine hydrochloride; with phenylhydrazine acetate it yields the bisphenylhydrazone of iminodiacetaldehyde,  $\text{NH}(\text{CH}_2 \cdot \text{CH} \cdot \text{N} \cdot \text{NHPh})_2$ ;

with semicarbazide it gives the hydrochloride of morpholylsemicarbazone, annexed formulæ, which with dilute hydrochloric acid is slowly converted at the ordinary temperature into pyrazine and carbamide with loss of water, and with hydrazine or hydroxylamine it furnishes products extremely soluble in water, which pass into pyrazine at 0°. These reactions lead to the conclusion that in pyrazine the two nitrogen atoms are directly linked together, thus :



Diacetalylhydrazine also yields pyrazine when treated with hydrochloric acid, but the mechanism of this reaction is obscure, owing to the occurrence of a second reaction which has not yet been explained.

By using a modification of the process previously described for the preparation of acetalylamine (Wolff, *loc. cit.*, Abstr., 1893, i, 612), a mixture of di- and tri-acetalylamines with some acetalylamine is obtained, which is separated by fractional distillation. *Triacetalylamine*,  $\text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_3$ , is a yellow liquid of a faintly aromatic odour. It has b. p. 175°/11 mm. (without decomposition), 302—304°/745 mm. (slight decomp.),  $D_4^{20}$  0.957, and  $n_D^{20}$  1.4322. It dissolves in 25 parts of water at 0° and 76 parts at 19°. The *platini-chloride* forms brownish-red to orange needles, m. p. 136° (decomp.); the *aurichloride* and *mercurichloride* are oils. *Trimorpholine*,  $\text{C}_6\text{H}_9\text{O}_3\text{N}$ , forms large, colourless, monoclinic crystals, which turn yellow at 180° and decompose at 210—220°. The base is very slowly attacked by hydroxylamine with the formation of a small amount of glyoxime. The *hydrochloride*, decomp. 255—260°, *mercurichloride*, decomp. above 260°, *aurichloride*, decomp. 220°, *picrate*, m. p. 210° (decomp.), *nitrate*, decomp. 240°, *oxalate*, decomp. above 220°, *methiodide*, decomp. above 270°, *methochloride*, decomp. 308°, and the following double salts of the latter: *mercury*, m. p. 270°, *gold*, m. p. 290°, and *platinum*, decomp. above 270°, are described. The *ammonium* base, prepared from the methiodide, forms a white, leafy, crystalline mass, m. p. 76—78°.

Diacetalylamine is a liquid of faint aromatic odour, b. p. 133°/9 mm., 260—262°/745 mm., decomposing slightly at the latter temperature. It has  $D_4^{20}$  0.938 and  $n_D^{20}$  1.4248. It forms a *benzoyl* and an *acetyl* derivative, b. p. 290°. The *hydrogen oxalate*, by means of which the base can be separated from triacetalylamine, forms colourless leaves, m. p. 174—175° (decomp.). The *nitroso-derivative*,  $\text{NO} \cdot \text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2$ , is a pale greenish-yellow oil of a faint, agreeable odour, b. p. 162°/13 mm.,  $D_4^{20}$  1.014,  $n_D^{20}$  1.4397. It does not give Liebermann's reaction. On reduction with zinc dust and acetic acid, it yields *diacetalylhydrazine*,  $\text{NH}_2 \cdot \text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2$ , a colourless, viscid oil of faint aromatic odour, b. p. 149°/10 mm.,  $D_{15}^{20}$  0.972, which gives a viscid *benzoyl* derivative, and forms a viscid compound with *p*-nitrobenzaldehyde. The *hydrochloride*, white needles, m. p. 75—76°, and *hydrogen oxalate*, small, white needles, m. p. 104—105°, are

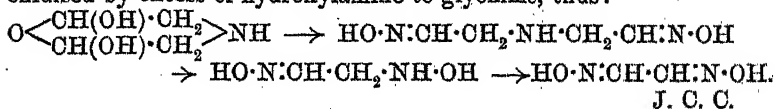
described. *Diacetalylsemicarbazide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N}[\text{CH}_2 \cdot \text{CH}(\text{OEt})_2]_2$ , forms small, white needles, m. p.  $96^\circ$ .

*Dihydroxymorpholine hydrochloride* forms white, microscopic needles or tablets, m. p.  $124^\circ$ . The corresponding *aurichloride* crystallises in small, brownish-yellow prisms or tablets, m. p.  $130^\circ$  (decomp.). *Dihydroxythiomorpholine hydrochloride*,



forms colourless or pale yellow prisms, m. p.  $113$ — $114^\circ$  (decomp.). The *bisphenylhydrazone* of *iminodiacetaldehyde* crystallises in pale yellow, quadratic tablets or in small prisms, m. p.  $114^\circ$ . The *hydrochloride*, colourless, microscopic needles, m. p.  $134$ — $135^\circ$ , *nitrate*, pale yellow, crystalline powder, m. p.  $140^\circ$ , and *picrate*, deep red, crystalline powder, m. p.  $132$ — $133^\circ$  (decomp.), are described. *Morpholylsemicarbazone* is an amorphous mass. The *nitrate*,  $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2 \cdot \text{HNO}_3 \cdot 2\text{H}_2\text{O}$ , a brownish-white, crystalline powder, m. p.  $178^\circ$  (decomp.), *picrate*, crystallising with  $2\text{H}_2\text{O}$ , yellow needles or leaflets, m. p.  $153$ — $154^\circ$  (decomp.), *hydrochloride*, crystallising with  $2\text{H}_2\text{O}$ , white powder, decomp. at  $187$ — $190^\circ$ , *mercurichloride*, aggregates of colourless prisms, m. p.  $168$ — $169^\circ$  (decomp.), and *aurichloride* are described. By treating morpholylsemicarbazone with boiling 20% hydrochloric acid, pyrazine is obtained; the aurichloride, m. p.  $247^\circ$  (decomp.), on crystallisation from boiling water loses  $\text{HCl}$ , yielding the salt,  $\text{C}_4\text{H}_4\text{N}_2 \cdot \text{AuCl}_3$ , golden-yellow leaflets, m. p.  $212$ — $214^\circ$  (compare Abstr., 1893, i, 612).

Pyrazine may be prepared in a 78% yield direct from diacetalylamine by treating the hydrochloride with hydroxylamine hydrochloride. By the action of hydroxylamine hydrochloride on dihydroxymorpholine, a 70% yield of pyrazine is obtained, together with a small amount of glyoxime, which is also formed directly from diacetalylamine and hydroxylamine; it is therefore probable that in the interaction between dihydroxymorpholine and hydroxylamine the dioxime of iminoacetaldehyde is first formed, which is then hydrolysed and oxidised by excess of hydroxylamine to glyoxime, thus:



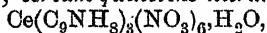
**Double Nitrates and Double Sulphates of the Rare Earths.** A. KOLB [with G. MELZER, A. MERCKLE, and C. TEUFFEL] (*Zeitsch. anorg. Chem.*, 1908, 60, 123—133. Compare Wyruboff, Abstr., 1908, ii, 385). —The double nitrates were prepared by evaporating aqueous solutions of the components and recrystallising from absolute alcohol. *Thorium diethylamine nitrate*,  $\text{Th}(\text{NH}_4\text{Et}_2)_2(\text{NO}_3)_6$ , occurs in transparent, rhombic crystals, m. p. very low. *Thorium pyridine nitrate*,



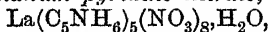
forms colourless, pointed leaflets, m. p.  $135^\circ$ . The corresponding *quinoline* compound,  $\text{Th}(\text{C}_9\text{NH}_7)_4(\text{NO}_3)_8$ , also forms colourless, spear-shaped crystals, m. p.  $135^\circ$ . Thorium nitrate reacts with antipyrine as free base even in the presence of excess of nitric acid. When 1 mol. of thorium nitrate and 4 mols. of antipyrine interact in nitric

acid solution, the compound,  $2\text{Th}(\text{NO}_3)_4 \cdot 5\text{C}_{11}\text{H}_{12}\text{ON}_2$ , is formed; in the absence of acid, the same compound with  $4\text{H}_2\text{O}$  is obtained. When 8 mols. of antipyrine are used, the compound,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{C}_{11}\text{H}_{12}\text{ON}_2$ , is obtained, and the same compound is formed when solid thorium nitrate (2 grams) is added to fused antipyrine (6 grams).

*Cerium pyridine nitrate*,  $\text{Ce}(\text{C}_5\text{NH}_6)_5(\text{NO}_3)_8 \cdot \text{H}_2\text{O}$ , forms large, colourless plates, m. p.  $82.5^\circ$ ; *cerium quinoline nitrate*,

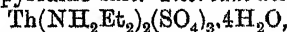


prismatic crystals, m. p.  $165^\circ$ ; *cerium piperidine nitrate*, lustrous, rhombic crystals; *lanthanum pyridine nitrate*,

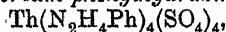


colourless, monoclinic crystals, m. p.  $91.5^\circ$ ; *lanthanum quinoline nitrate*,  $\text{La}(\text{C}_9\text{NH}_8)_3(\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ , m. p.  $153^\circ$ .

The majority of the double sulphates were prepared by boiling the solid rare earth sulphate with an aqueous solution of the other sulphate until a clear solution was obtained; the separation of the double salt was in some cases brought about by the addition of absolute alcohol. *Thorium pyridine sulphate*,  $\text{Th}(\text{C}_5\text{NH}_6)_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ , occurs in colourless, microscopic leaflets, and is readily split up into its components by water. *Thorium quinoline sulphate*,  $\text{Th}(\text{C}_9\text{NH}_8)_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ , behaves in all respects like the pyridine salt. *Thorium diethylamine sulphate*,

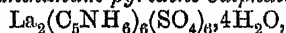


and *thorium ethylamine sulphate*,  $\text{Th}(\text{NH}_2\text{Et})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ , occur in colourless crystals. *Thorium phenylhydrazine sulphate*,



occurs in small, slightly yellow crystals, which are very stable.

*Cerium pyridine sulphate*,  $\text{Ce}_2(\text{C}_5\text{NH}_6)_6(\text{SO}_4)_6 \cdot 3\text{H}_2\text{O}$ , needles, *cerium quinoline sulphate*, probably  $\text{Ce}_2(\text{SO}_4)_3 \cdot 6\text{C}_9\text{NH}_8 \cdot 4\text{H}_2\text{SO}_4 \cdot 17\text{H}_2\text{O}$ , *cerium hydrazine sulphate*, lustrous crystals, *cerium hydroxylamine sulphate*, microscopic leaflets, *lanthanum pyridine sulphate*,



lustrous, columnar crystals, *lanthanum quinoline sulphate*, small, columnar crystals, and *lanthanum hydrazine sulphate*, small leaflets, have also been prepared.

G. S.

**Organic Mercury Compounds.** EINAR BILLMANN (*Ber.*, 1908 41, 4340—4341. Compare Schrauth and Schoeller Abstr., 1908, i, 617).—A claim for priority: the alkyl mercuridimalonates have been obtained previously (Abstr., 1902, i, 665). W. R.

**Nitration of Toluene.** ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 248—256. Compare Abstr., 1905, i, 272; Nölting and Wild, Abstr., 1885, 973; Loesner, Abstr., 1895, i, 214; Holdermann, Abstr., 1906, i, 439; Friswell, Abstr., 1908, i, 332).—An investigation on the composition of the product obtained when toluene is nitrated at various temperatures by adding nitric acid (D 1.475) to the hydrocarbon. The percentages of the isomeric mononitrotoluenes present in the nitration product were ascertained by determining its density and initial solidifying point and comparing with mixtures of known composition. In this way, it was found that the product obtained by nitrating at  $-30^\circ$ ,  $0^\circ$ ,  $30^\circ$ , and  $60^\circ$  contained

41.7, 40.9, 39.9, and 38.5% of *p*-nitrotoluene; 55.6, 56.0, 56.9, and 57.5% of *o*-nitrotoluene, and 2.7, 3.1, 3.2, and 4.0% of *m*-nitrotoluene respectively.  
W. H. G.

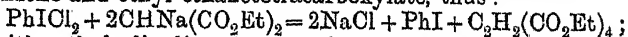
**Nitration of *p*-Chlorotoluene.** ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 257—260. Compare preceding abstract).—The initial solidifying points and densities of mixtures of 4-chloro-2-nitrotoluene (solidifying point 38.2°,  $D^{20}_D$  1.2559) and 4-chloro-3-nitrotoluene (solidifying point 5.8°,  $D^{20}_D$  1.2296) have been determined; mixtures containing 57.0, 44.7, 34.8, 29.8, 24.1, 17.5, 14.1, and 6.6% of the former compound commence to solidify at 9.7°, 1.4°, -6.3°, -7.2°, -4.1°, -0.5°, 0.4°, and 4.5° respectively; mixtures having  $D^{20}_D$  1.2477 and 1.2364 contain respectively 57 and 17.5% of 4-chloro-2-nitrotoluene.

Since the product obtained by acting on *p*-chlorotoluene at 0° with about four times its weight of nitric acid ( $D$  1.48) commences to solidify at 10.2° and has  $D^{20}_D$  1.2481, it must contain 58% of 4-chloro-3-nitrotoluene and 42% of 4-chloro-2-nitrotoluene. The product obtained by nitrating at 30° and 60° contains polynitro-4-chlorotoluenes.

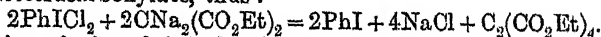
W. H. G.

**Some Reactions of Phenyl Iodochloride and Iodobenzene Acetate.** HERBERT HENRY HODGSON (*Proc. Camb. Phil. Soc.*, 1908, 14, 547—556).—Unsuccessful attempts have been made to prepare compounds containing the grouping  $\text{:C:I:C:}$  or  $\text{:}\overset{\text{I}}{\underset{\text{C}}{\text{C}}}\text{:}$ , possibly because suitable conditions for isolating the substances were not employed.

Phenyl iodochloride interacts with ethyl sodiomalonate, forming iodobenzene and ethyl ethanetetracarboxylate, thus:



and with ethyl disodiomalonate, forming iodobenzene and ethyl ethylenetetracarboxylate, thus:



The action of phenyl iodochloride is, therefore, analogous to that of iodine on the sodium derivatives of ethyl malonate (compare Bischoff, *Abstr.*, 1885, 244; 1896, i, 469; Blank and Samson, *Abstr.*, 1899, i, 484). Similarly, iodine acts on ethyl sodiocyanoacetate, forming ethyl dicyanosuccinate, which is obtained in good yield. Iodobenzene acetate behaves like phenyl iodochloride towards ethyl sodio- and disodio-malonate.

Phenyl iodochloride and iodobenzene acetate react with ethyl sodiocyanoacetate in a similar manner, yielding iodobenzene and ethyl dicyanosuccinate.

Diphenyliodonium iodide and ethyl sodiomalonate apparently do not interact either at the ordinary temperature or at 100°. W. H. G.

**Chlorides of Aromatic Sulphinic Acids.** THOMAS P. HILDITCH and SAMUEL SMILES (*Ber.*, 1908, 41, 4113—4116).—The reaction between phenolic ethers, thionyl chloride, and aluminium chloride takes place in three stages (Smiles and Le Rossignol, *Trans.*, 1906, 39, 696; 1908, 93, 745; Knoevenagel and Kenner, *Abstr.*, 1908, i,

970), but hitherto the aromatic sulphinyl chloride produced in the first step has not been isolated. The authors have now obtained aromatic sulphinyl chlorides by the action of an excess of thionyl chloride on the sulphinic acids at the ordinary temperature. *Benzenesulphinyl chloride*,  $\text{PhSOCl}$ , has m. p.  $38^\circ$ . *p-Toluenesulphinyl chloride*,  $\text{C}_7\text{H}_7\text{SOCl}$ , has m. p.  $54-58^\circ$ . *4-Methoxytoluene-3-sulphinyl chloride* has m. p.  $70-73^\circ$ .  
C. S.

**Preparation of Diphenylmethane.** ALEXANDER M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1376—1379).—The author has investigated further the interaction of benzene and formaldehyde in presence of concentrated sulphuric acid (compare Abstr., 1904, i, 242). For the preparation of diphenylmethane, the glacial acetic acid employed may be replaced by water, provided that the proportions of formaldehyde and sulphuric acid are suitably adjusted.

T. H. P.

**Fluorene Perhydride : Reply to Spiegel.** JULIUS SCHMIDT and ERNST FISCHER (*Ber.*, 1908, 41, 4227—4230).—In view of Spiegel's statement (Abstr., 1908, i, 331) that, contrary to Schmidt and Mezger's view (*ibid.*, i, 16) of the non-existence of Liebermann's fluorene perhydride (Abstr., 1889, 719), the compound can actually be prepared, the authors have repeated Liebermann and Spiegel's work and maintain that the substance obtained is really the decahydride.

J. C. C.

**Preparation of 9:10-Dihydrophenanthrene.** JULIUS SCHMIDT and ERNST FISCHER (*Ber.*, 1908, 41, 4225—4226).—Willstätter and Mayer's method of reduction with platinum and hydrogen (Abstr., 1908, i, 383) is very suitable for the preparation of dihydrophenanthrene. A brisk stream of pure hydrogen is led into a boiling ethereal solution of phenanthrene in the presence of platinum black. After six to eight hours, the solution is filtered and evaporated, when the residue consists of almost pure 9:10-dihydrophenanthrene. The reduction may also be carried out at the ordinary temperature, but in this case requires about two days (for 5 grams of phenanthrene).

J. C. C.

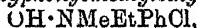
**Hydrogenation of Triphenylmethane. Tricyclohexylmethane.** MARCEL GODCHOT (*Compt. rend.*, 1908, 147, 1057—1059).—The ultimate reduction product obtained by submitting triphenylmethane to the hydrogenisation process of Sabatier and Senderens (Abstr., 1901, i, 459) is *tricyclohexylmethane*,  $\text{CH}(\text{C}_6\text{H}_{11})_3$ , a colourless liquid with an aromatic odour, b. p.  $140^\circ/20\text{ mm.}$ ,  $D^{18}_4$  0.8406. This compound is sparingly soluble in alcohol and acetic acid, but very soluble in ether and benzene; these solutions are not fluorescent. It develops a brown coloration with sulphuric acid, and yields hydrogen bromide and a bromo-derivative with bromine. *Phenyl-dicyclohexylmethane*,  $\text{C}_{19}\text{H}_{28}$ , b. p.  $210-212^\circ/20\text{ mm.}$ ,  $D^{18}_4$  0.9894, was obtained at an intermediate stage in the preparation, but not in a state of purity.

W. O. W.

**The Action of Dichloroacetic Acid on Aniline and its Homologues.** GUSTAV HELLER (*Ber.*, 1908, 41, 4264—4266. Compare Abstr., 1904, i, 730).—A reply to Ostromisslensky (Abstr., 1908, i, 82, 888). It has not been found possible to isolate phenylmesatin from the products obtained by the action of dichloroacetic acid on aniline; the chief product is the diamino-acid, m. p. 98°. The author does not agree with Ostromisslensky's view that the compound  $C_{14}H_{14}O_2N_2$  is dianilinoacetic acid, as it is immediately decomposed by cold dilute alkalis. J. J. S.

**A New Kind of Asymmetry in the Nitrogen Atom.** JAKOB MEISENHEIMER (*Ber.*, 1908, 41, 3966—3976).—It is theoretically possible to have two forms of a quinevalent nitrogen compound in which there are four different radicles, related as object and image, but so far all attempts to resolve such compounds have resulted in failure. Further, this possibility exists in the amino-oxides, and experiments were undertaken with the object of resolving methylethylaniline oxides into optical isomerides.

Methylethylaniline, on being stirred for three days with hydrogen peroxide at 60—70°, is converted into the oxide, which is purified by conversion into the picrate. This, on treatment with hydrochloric acid, yields racemic *hydroxyphenylmethylethylammonium chloride*,



which crystallises in colourless, hygroscopic needles from a mixture of alcohol and ether; m. p. 122—124° (decomp.). The compound is strongly acid; its *picrate*,  $C_{15}H_{16}O_8N_4$ , has m. p. 147—148° (decomp.). The free *base* obtained from the chloride by baryta is a very hygroscopic solid, and decomposes slowly. The chloride on treatment with silver *d*-bromocamphorsulphonate is resolved into two optical antipodes, the *l*-hydroxyphenylmethylethylammonium-*d*-bromocamphorsulphonate,  $C_{19}H_{28}O_8NBrS$ , being the less soluble, decomp. 167—168°,  $[\alpha]_D + 50^\circ$ ,  $[M]_D 231—235^\circ$ ; the *d*-salt has m. p. 151—153° (decomp.),  $[\alpha]_D + 68^\circ$ ,  $[M]_D 311—315^\circ$ .

The *d*-picrate, m. p. 147—148° (decomp.), when treated with hydrochloric acid and ether, is converted into the *d*-chloride, which crystallises in hygroscopic prisms, m. p. 90—95°,  $[M]_D + 32^\circ$ . The *l*-chloride, obtained in a similar manner, has  $[M]_D - 41^\circ$ , the calculated value from the bromocamphorsulphonate being  $\pm 40^\circ$ .

If the active chlorides be decomposed by baryta water free from carbonate, the bases are obtained, and the  $[M]_D$ 's of the solutions decrease from  $-41^\circ$  to  $-25^\circ$  and  $+32^\circ$  to  $+20^\circ$  respectively, a result probably not due to racemisation, as the original value is re-obtained on acidification with hydrogen chloride. Further, these values are not altered after three days. The free bases are obtained as very hygroscopic oils after removal of the barium chloride, and have not yet been isolated in the solid condition. It is, therefore, uncertain whether they possess the formula:  $O \cdot NMeEtPh$  or  $NMeEtPh(OH)_2$ .

W. R.

**3:5-Dibromoaceto-*p*-toluidide and its Nitro-derivatives.** FRANZ KUNCKELL (*Ber.*, 1908, 41, 4111—4112).—Ulffers and

von Janson's 3:5-dibromoaceto-*p*-toluidide (Abstr., 1894, i, 719) is conveniently obtained by heating aceto-*p*-toluidide with somewhat less than the calculated quantity of bromine in chloroform for four hours at 90—100°. With fuming nitric acid, it yields 3:5-dibromo-2-nitroaceto-*p*-toluidide, m. p. 238°, whilst in the presence of concentrated sulphuric and fuming nitric acids, 3:5-dibromo-4:6-dinitroaceto-*p*-toluidide, m. p. 265—267°, is obtained, from which boiling aniline eliminates one atom of the halogen. C. S.

*cyclo*Hexanol. G. CHAVANNE and Mlle. B. VAN ROELEN (*Bull. Soc. chim. Belg.*, 1908, 22, 410—413. Compare Mascarelli, Abstr., 1907, ii, 602, 936; 1908, i, 527).—Cryoscopic determinations of the molecular weights, using *cyclo*hexanol as a solvent, are rendered difficult by the smallness or absence of the phenomenon of superfusion, and by the slow rate of crystallisation. Experiments made with nineteen organic compounds show that the latter can be divided into two groups: (1) including aromatic hydrocarbons composed of several nuclei or having complex side-chains, such as naphthalene, *m*-xylene, *p*-xylene, cymene, diphenyl, and acenaphthene, which produce a molecular depression of 61—62 (water, 1·85); and (2) all other types of organic compound which either do not obey the Blagden-Rüdorff law, or give molecular depressions less than 61. Thus nitrobenzene gives the value 53, toluene 40, chloroform 25, ethyl alcohol 34·5, methyl alcohol 28, lactic acid 40, isobutyric acid 33, *cyclo*hexanone 31, *cyclo*hexene 23, and *cyclo*hexane 11. The conclusion is drawn that the normal molecular depression for *cyclo*hexanol is 61·5. Substituting this value in van't Hoff's formula ( $K = 0\cdot02T^2/L$ ) gives 2·8 Cal. as the value for the heat of fusion ( $L$ ), whilst a direct determination of the latter constant gives the value 3 Cal.

The anomalous results obtained in cryoscopic determinations with *cyclo*hexanol may be due either to the associating power of this solvent or to its capacity for forming solid solutions.

*cyclo*Hexanol easily loses water with the production of *cyclo*hexene; thus when heated at 80° with an equal molecular quantity of methyl sulphate, 40 grams of the alcohol give 26 grams of *cyclo*hexene. Similarly, when boiled over alumina or silica, the vapour of *cyclo*hexanol is wholly converted into *cyclo*hexene and water. E. H.

2:4-Dinitro- $\alpha$ -naphthol. FRITZ ULLMANN and WALTER BRUCK (*Ber.*, 1908, 41, 3932—3939).—A continuation of the work of Ullmann and Náday (Abstr., 1908, i, 525). The interaction of *p*-toluenesulphonyl chloride, diethylaniline, and 2:4-dinitro- $\alpha$ -naphthol furnishes at the ordinary temperature the dinitronaphthyl ester of *p*-toluenesulphonic acid, and at a higher temperature 1-chloro-2:4-dinitronaphthalene. Both compounds react readily with bases, giving the corresponding  $\alpha$ -naphthylamine derivatives, and the reactions proceed so smoothly that it is unnecessary to isolate the intermediate compounds in the preparation of the latter.

1-Chloro-2:4-dinitronaphthalene crystallises in large, yellow needles, m. p. 146·5° (corr.). 2:4-Dinitro- $\alpha$ -naphthyl *p*-toluenesulphoante,  $C_{10}H_5(NO_2)_2 \cdot O \cdot SO_2 \cdot C_6H_5$ , forms large, pearly, almost colourless leaflets, m. p. 159·5° (corr.).

By warming a mixture of dinitronaphthol, pyridine, and toluene-sulphonyl chloride, there is formed 2:4-dinitro- $\alpha$ -naphthylpyridinium toluenesulphonate,  $C_{27}H_{17}O_7N_3S$ , in shining leaflets, m. p.  $205^\circ$  (decomp.). When either the ester or the chloro-derivative mentioned above is treated with ammonia, 2:4-dinitro- $\alpha$ -naphthylamine is produced, and with dimethylamine there is formed 2:4-dinitro- $\alpha$ -naphthyl-dimethylamine,  $C_{10}H_5(NO_2)_2 \cdot NMe_2$ , which crystallises in orange-red needles, m. p.  $88^\circ$ .

2:4-Dinitro- $\alpha$ -naphthylbenzylamine,  $C_{10}H_5(NO_2)_2 \cdot NH \cdot CH_2Ph$ , prepared by warming chlorodinitronaphthalene with benzylamine in alcoholic solution, forms orange-red needles, m. p.  $139^\circ$  (corr.). Phenyl-2:4-dinitro- $\alpha$ -naphthylamine,  $C_{10}H_5(NO_2)_2 \cdot NHPh$ , prepared either from the ester or the chloro-derivative, or from dinitronaphthol without the isolation of the intermediate compound, crystallises in large, orange-red, glistening plates, m. p.  $180^\circ$  (corr.).

On reduction with zinc dust, alcohol, and ammonium chloride, it yields phenyl-2:4-diamino- $\alpha$ -naphthylamine, white, felted needles, m. p.  $190^\circ$  (corr.), which on distillation with lead oxide gives 6-amino-naphthaphenazine.

2-Hydroxyphenyl-2:4-dinitro- $\alpha$ -naphthylamine,  
 $C_{10}H_5(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot OH$ ,

prepared by condensing the ester with *o*-aminophenol, forms orange-red, felted needles, m. p.  $178^\circ$  (corr.). 2:4-Dinitro- $\alpha$ -naphthyl methyl ether, prepared by the action of sodium methoxide on the chloro-derivative, forms yellow needles, m. p.  $97^\circ$ .

The ethyl ether is obtained in a similar manner.

J. C. C.

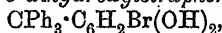
Action of Chlorine, Bromine, and Nitric Acid on *p*-Hydroxy-tetraphenylmethane. THEODOR ZINCKE and E. WUGK (*Annalen*, 1908, 363, 284—301. Compare this vol., i, 23).—3:5-Dibromo-*p*-hydroxytetraphenylmethane,  $CPh_3 \cdot C_6H_2Br_2 \cdot OH$ , prepared by brominating the parent substance, crystallises in white needles or leaflets, m. p.  $168^\circ$ ; it forms a sodium salt and an acetate,  $C_{27}H_{20}O_2Br_2$ , white needles, m. p.  $177^\circ$ , and on treatment with bromine, it yields penta-bromo-*p*-hydroxytetraphenylmethane,  $C(C_6H_4Br)_3 \cdot C_6H_2Br_2 \cdot OH$ , in which the three added bromine atoms are probably in the para-position. This compound forms small, white crystals, m. p.  $267—271^\circ$ ; it forms an acetate,  $C_{27}H_{17}O_2Br_5$ , small, white needles, and, possibly, a perbromide, which was not, however, obtained pure.

3:5-Dichloro-*p*-hydroxytetraphenylmethane,  $CPh_3 \cdot C_6H_2Cl_2 \cdot OH$ , prepared by chlorinating the parent substance, crystallises in small, white needles, m. p.  $135^\circ$ ; the acetate,  $C_{27}H_{20}O_2Cl_2$ , forms large, white needles, m. p.  $180^\circ$ .

3-Nitro-*p*-hydroxytetraphenylmethane,  $CPh_3 \cdot C_6H_3(NO_2) \cdot OH$ , prepared by adding nitric acid, D 1.4, to a solution of the parent substance in glacial acetic acid, or by adding sodium nitrite to an ethereal solution containing water and acetic acid, forms yellow leaflets or dark yellow, compact crystals, m. p.  $183—184^\circ$ ; the alkali salts are brownish-red; the acetate,  $C_{27}H_{21}O_4N$ , forms small, yellow needles, m. p.  $152^\circ$ . 3-Bromo-5-nitro-*p*-hydroxytetraphenylmethane,  $CPh_3 \cdot C_6H_2Br(NO_2) \cdot OH$ , prepared by adding sodium nitrite to a glacial acetic acid solution of

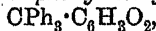
the dibromo-compound or by warming the latter solution with nitric acid, crystallises in yellow needles, m. p. 188°; it forms brownish-red alkali salts; the acetate,  $C_{27}H_{30}O_4NBr$ , crystallises in white needles, m. p. 169—170°.

6-Bromo-4-triphenylmethyl-o-benzoquinone,  $CPh_3 \cdot C_6H_2O_2Br$ , prepared by adding nitric acid, D 1.5, to a glacial acetic acid solution of dibromo-*p*-hydroxytetraphenylmethane at 40°, crystallises in red needles with a golden lustre, m. p. 230°; on reduction with hydriodic acid, it yields 3-bromo-4:5-dihydroxytetraphenylmethane,



which crystallises in almost white needles, m. p. 175°; the diacetate forms leaflets, m. p. 135—136°. 6-Chloro-4-triphenylmethyl-o-benzoquinone,  $CPh_3 \cdot C_6H_2O_2Cl$ , prepared similarly from the dichloro-compound, crystallises in red needles with a golden lustre, m. p. 229°; at the same time is formed chloronitro-*p*-hydroxytetraphenylmethane, large, yellow crystals, m. p. 154°. On reduction, the quinone furnishes 3-chloro-4:5-dihydroxytetraphenylmethane,  $CPh_3 \cdot C_6H_2Cl(OH)_2$ , crystallising in white needles, m. p. 190—191°; it is oxidised by nitric acid to the quinone, and forms an acetate.

3:4-Dihydroxytetraphenylmethane,  $CPh_3 \cdot C_6H_3(OH)_2$ , prepared by the condensation of triphenylcarbinol with catechol, crystallises in white needles and leaflets, m. p. 262—263°; with bromine it yields 3-bromo-4:5-dihydroxytetraphenylmethane; it forms a diacetyl derivative, white needles, m. p. 197—198°, and when oxidised with nitric acid, D 1.5, it gives 4-triphenylmethyl-o-benzoquinone,



crystallising in dull red needles with a green, metallic lustre, m. p. 217°. J. C. C.

Styphnic Acid. FRITZ ULLMANN and WALTER BRUCK (*Ber.*, 1908, 41, 3939—3940).—Styphnic acid combines with 1 mol. of diethylaniline to form a salt, which crystallises in yellow needles, m. p. 159°. When styphnic acid, diethylaniline, and *p*-toluenesulphonyl chloride are warmed together, the diethylaniline salt of 2:4:6-trinitro-3-hydroxyphenyl *p*-toluenesulphonate,  $OH \cdot C_6H(NO_2)_3 \cdot O \cdot SO_2 \cdot C_6H_4 \cdot NEt_2Ph$ , is obtained. This forms small, yellow plates, m. p. 164° (decomp.); on boiling with alcoholic hydrogen chloride, styphnic acid is regenerated, and when treated with aniline it yields 2:4:6-trinitro-3-hydroxydiphenylamine,  $OH \cdot C_6H(NO_2)_3 \cdot NHPh$ , crystallising in orange-yellow needles, m. p. 162° (corr.). J. C. C.

Action of Bromine on the Alkyl and Aryl Derivatives of Di-*p*-hydroxydiphenylmethane. THEODOR ZINCKE (*Annalen*, 1908, 363, 246—283).—The author has extended his work on the action of bromine and alkyl and aryl derivatives of di-*p*-hydroxydiphenylmethane (Zincke and Krügener, *Abstr.*, 1904, i, 401; Zincke and Grüters, *Abstr.*, 1906, i, 172; Zincke, *ibid.*, 737; Zincke and Goldemann, *Abstr.*, 1908, i, 780) to the cases of di-*p*-hydroxy-di- $\alpha$ -phenylethane, -tri- $\alpha$ -phenylethane, -tetraphenylmethane, and -triphenylmethane.

[With K. HENKE].—Four, six, or eight atoms of bromine can be introduced into the molecule of di-*p*-hydroxydi- $\alpha$ -phenylethane (prepared

according to Lunjak's method, Abstr., 1904, i, 495). The resulting compounds are normal phenols and soluble in alkali. By the action of sodium nitrite in glacial acetic acid solution, an atom of bromine is replaced by the nitro-group. 3:5:3':5'-Tetrabromodi-*p*-hydroxydi-*a*-phenylethane,  $\text{CHMe}(\text{C}_6\text{H}_2\text{Br}_2\cdot\text{OH})_2$ , prepared by the action of bromine on the parent phenol dissolved in glacial acetic acid, forms nodular crystals, m. p. 140—141°; the diacetate,  $\text{C}_{18}\text{H}_{14}\text{O}_4\text{Br}_4$ , crystallises in white leaflets, m. p. 130—131°. 3:3'-Dibromo-5:5'-dinitrodi-*p*-hydroxydi-*a*-phenylethane,  $\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_2\text{Br}_2$ , is prepared by adding solid sodium nitrite to a solution of the tetrabromo-compound in glacial acetic acid; it forms compact, yellow crystals, m. p. 172°, and yields a sparingly soluble red salt with alkali; the diacetate forms yellowish white, compact crystals, m. p. 174—175°. When the tetrabromo-compound is heated with bromine and carbon tetrachloride in a sealed tube at 100°, there is formed 3:5:6:3':5':6'-hexabromodi-*p*-hydroxydi-*a*-phenylethane,  $\text{C}_{14}\text{H}_8\text{O}_2\text{Br}_6$ , in white leaves or compact crystals, m. p. 169—170°; the diacetate,  $\text{C}_{18}\text{H}_{12}\text{O}_4\text{Br}_6$ , crystallises in white needles, m. p. 182—183°. 2:5:2':5'-Tetrabromo-3:3'-dinitrodi-*p*-hydroxydi-*a*-phenylethane,  $\text{C}_{14}\text{H}_8\text{O}_6\text{N}_2\text{Br}_4$  (constitution not quite certain), formed by the action of sodium nitrite on a solution of the hexabromo-derivative in glacial acetic acid, crystallises in yellow needles, m. p. above 145° (decomp.); the diacetate,  $\text{C}_{18}\text{H}_{12}\text{O}_8\text{N}_2\text{Br}_4$ , forms yellow needles, m. p. 123°.

2:3:5:6:2':3':5':6'-Octabromodi-*p*-hydroxydi-*a*-phenylethane,  $\text{C}_{14}\text{H}_6\text{O}_2\text{Br}_8$ , prepared by heating the hexabromo-compound with bromine at 160—180°, crystallises in large, transparent prisms or in colourless, stout needles, m. p. 227—228°; the diacetate,  $\text{C}_{18}\text{H}_{10}\text{O}_4\text{Br}_8$ , forms compact, white needles, m. p. 205—206°. 2:3:6:2':3':6'-Hexabromo-5:5'-dinitrodi-*p*-hydroxydi-*a*-phenylethane,  $\text{C}_{14}\text{H}_6\text{O}_6\text{N}_2\text{Br}_6$ , prepared by the action of sodium nitrite on a glacial acetic acid solution of the octabromo-compound, crystallises in yellow leaflets, m. p. 233° (decomp.); the diacetate,  $\text{C}_{18}\text{H}_{10}\text{O}_8\text{N}_2\text{Br}_6$ , is a crystalline powder, m. p. 252—254°.

Of the three bromo-derivatives of di-*p*-hydroxydi-*a*-phenylethane, only the tetrabromo-compound undergoes fission under the influence of bromine; the reaction proceeds at the ordinary temperature, with the formation of  $\alpha\beta$ -3:5-tetrabromo-*o*-*p*-ethylphenol, m. p. 124° (Zinke and Leisse, Abstr., 1902, i, 615) and 2:3:4:6-tetrabromophenol (m. p. 112—113° instead of 118° and 120°, as given in the literature); the acetate of the latter forms white leaflets or stout needles, m. p. 104—105°.

Tetrabromodi-*p*-hydroxydi-*a*-phenylethane, when treated in glacial acetic acid solution with nitric acid, D 1.4, gives 2:6-dibromo-4-nitrophenol and a substance,  $\text{C}_8\text{H}_6\text{O}_6\text{N}_2\text{Br}$ , crystallising in yellow needles, m. p. 102—103°, which is, perhaps, a bromodinitroethyl-*p*-benzoquinone; if, however, the tetrabromo-derivative is added to nitric acid, D 1.5, there are formed 2-bromo-4:6-dinitrophenol and 2:6-dibromo-*p*-benzoquinone.

Hexabromodi-*p*-hydroxydi-*a*-phenylethane is decomposed by nitric acid, D 1.4, into a quinone-like substance, which could not be purified, and a small amount of 2:3(or 2:5)-dibromo-5(or 3)-nitro-*p*-ethyl-

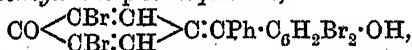
*phenol*,  $C_6H_7O_3NBr_2$ , crystallising in yellow needles, sintering at  $145^\circ$ , m. p.  $160^\circ$  (decomp.); the *acetate*,  $C_{10}H_9O_4N_2Br_2$ , forms yellow needles, m. p.  $96-98^\circ$ .

Octabromodi-*p*-hydroxydi- $\alpha$ -phenylethane is decomposed by nitric acid, D 1.4, but only a small amount of a substance, crystallising in yellow leaflets, m. p.  $233^\circ$  (decomp.), and giving a yellowish-red, sparingly soluble alkali salt, could be isolated; it is suggested that the substance may be 2:5:6-tribromo-5-nitro-4-hydroxyacetophenone.

[With W. WOLLENBERG.]—3:5:3':5'-*Tetrabromodi-p-hydroxytriphenylmethane*,  $CHPh(C_6H_4Br_2 \cdot OH)_2$ , prepared by the action of bromine on a chloroform solution of di-*p*-hydroxytriphenylmethane (Russanoff, Abstr., 1889, 1188), crystallises in colourless needles or prisms, m. p.  $160-161^\circ$ ; the *diacetate* forms white leaflets, m. p.  $165^\circ$ . The tetrabromo-compound is decomposed by nitric acid, D 1.5, into 2:6-dibromo-4-nitrophenol and benzaldehyde, and with sodium nitrite it yields 3:3'-dibromo-5:5'-dinitrodi-*p-hydroxytriphenylmethane*,



small, yellow needles, m. p.  $161^\circ$ , forming sparingly soluble, red alkali salts.  $\alpha$ -3:5:3':5'-*Pentabromodi-p-hydroxytriphenylmethane perbromide*,  $CBrPh(C_6H_4Br_2 \cdot OH)_2 \cdot Br_2$ , prepared by adding a slight excess of bromine to a glacial acetic acid solution of di-*p*-hydroxytriphenylmethane, forms dark red crystals with a green, metallic lustre, which, on boiling with acetone, yield 3:5:3':5'-*tetrabromo-4'-hydroxyphenylbenzylidene-p-benzoquinone*,



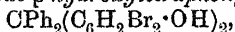
a micro-crystalline, dark brownish-red powder, remaining unmelted at  $270^\circ$ , and decomposing at a higher temperature; the sodium salt forms small, dark green needles with a metallic lustre. The quinone is reduced by hydriodic acid to tetrabromodi-*p*-hydroxytriphenylmethane; when boiled with acetone, water, and alkali hydroxide, it yields 3:5:3':5'-*tetrabromodi-p-hydroxytriphenylcarbinol*,  $CPh(C_6H_4Br_2 \cdot OH)_2 \cdot OH$ , a white, amorphous powder, and with methyl alcohol and sulphuric acid it forms the corresponding *methyl ether*,  $CPh(C_6H_4Br_2 \cdot OH)_2 \cdot OMe$ , a white, amorphous powder (compare Zincke and Krügener, *loc. cit.*; Zincke and Birschel, Abstr., 1908, i, 781). The perbromide described above readily loses bromine when triturated with acetone, yielding the  $\psi$ -form of  $\alpha$ -3:5:3':5'-*pentabromodi-p-hydroxytriphenylmethane*,  $CBrPh \cdot (C_6H_4Br_2 \cdot OH)_2$ , which is also obtained by treating the corresponding quinone with acetic-hydrobromic acid; it forms slender, white needles. When the quinone is treated with hydrochloric acid, the  $\psi$ -form of  $\alpha$ -chloro-3:5:3':5'-*tetrabromodi-p-hydroxytriphenylmethane* is obtained in slender, white needles.

[With E. WUGK.]—3:5:3':5'-*Tetrabromodi-p-hydroxytri- $\alpha$ -phenylethane*,  $CMePh(C_6H_4Br_2 \cdot OH)_2$ , prepared by mixing glacial acetic acid solutions of bromine and di-*p*-hydroxytri- $\alpha$ -phenylethane (m. p.  $187-188^\circ$ ; *diacetate*, white needles, m. p.  $179^\circ$ ), forms compact, colourless crystals, m. p.  $194^\circ$ ; the *diacetate* crystallises in white leaflets, m. p.  $96-98^\circ$ . With nitric acid, D 1.5, the compound yields 6-bromo-2:4-dinitrophenol.

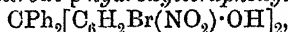
*p-Hydroxydiphenylmethylcarbinol*,  $CMePh(C_6H_4 \cdot OH) \cdot OH$ , obtained

on one occasion by the condensation of phenol with acetophenone, forms compact, white crystals, m. p. 186—187°; the *diacetate* crystallises in white needles, m. p. 178°. The carbinol yields with bromine a *tribromo-derivative*,  $C_{14}H_{11}O_2Br_3$ , forming white needles, m. p. 194°, and it condenses readily with phenol with the production of *di-p-hydroxytri- $\alpha$ -phenylethane*.

3 : 5 : 3' : 5'-*Tetrabromodi-p-hydroxytetraphenylmethane*,

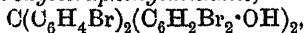


prepared by brominating *di-p-hydroxytetraphenylmethane* (Mackenzie, *Trans.*, 1901, 79, 1209), crystallises in compact, white needles, m. p. 202°; the *diacetate*,  $C_{20}H_{10}O_4Br_4$ , forms compact, white needles, m. p. 190°. When boiled with nitric acid, D 1.5, the tetrabromo-compound yields 6-bromo-2 : 4-dinitrophenol. and with sodium nitrite it gives 3 : 3'-*dibromo-5 : 5'-dinitrodi-p-hydroxytetraphenylmethane*,



yellow, glistening leaflets or transparent, brownish-yellow, rhombic tablets, m. p. 196—197°; the *diacetate*,  $C_{20}H_{10}O_8N_2Br_2$ , forms small, white needles, m. p. 166°.

*Hexabromodi-p-hydroxytetraphenylmethane*,



prepared by the action of bromine on the tetrabromo-compound, crystallises in stout, white needles, m. p. 286—290°; it forms a *sodium salt* and an *acetate*, white leaflets, m. p. 170°. J. C. C.

**Formation of Benzyl Ether.** RUDOLF WEGSCHEIDER (*Ber.*, 1908, 41, 4341).—The formation of benzyl ether from benzyl alcohol and a little sulphuric acid, regarded by Meisenheimer (*Abstr.*, 1908, i, 417) and Schroeter and Sondag (*Abstr.*, 1908, i, 497) as new, was first observed by the author (*Abstr.*, 1900, i, 657). W. R.

**Action of Phosphorus Pentachloride and Pentabromide on Mercaptans.** WILHELM AUTENRIETH and ALFRED GEYER (*Ber.*, 1908, 41, 4256—4258. Compare Vogt, *Annalen*, 1861, 119, 148).—Phenyl and benzyl mercaptans react with phosphorus pentachloride or pentabromide at -15°, giving quantitative yields of the corresponding disulphides, phosphorus trihalide, and hydrogen halide, for example:  $2PhSH + PCl_5 = S_2Ph_2 + PCl_3 + 2HCl$ . J. J. S.

**Phytosterol from South African Rubber.** N. H. COHEN (*Arch. Pharm.*, 1908, 246, 592—593).—The phytosterol previously described (*Abstr.*, 1908, i, 884) as similar to Schulze's *ischolesterol* has now been carefully compared with Schulze's original preparation, and corresponding derivatives of the two substances have also been examined. The results show that the two are identical. T. A. H.

**Electrolytic Dissociation Constants of *cyclo*Aliphatic Acids.** NICOLAI D. ZELINSKY and N. IZGARYSCHEFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1379—1388).—The authors have measured the dissociation constants for a number of cyclic acids, the following being the values of *K* obtained. *cyclo*Hexanecarboxylic (hexahydrobenzoic) acid, 0.00134; 1-methyl*cyclo*hexane-2-carboxylic (hexahydro-*o*-toluic)

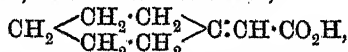
acid, solid *trans*-modification, 0.00205, liquid *cis*-modification, 0.00164; 1-methylcyclohexane-3-carboxylic (hexahydro-*m*-toluic) acid, 0.00128; 1-methylcyclohexane-4-carboxylic (hexahydro-*p*-toluic) acid, 0.00111; 1-methylcyclohexane-1-carboxylic acid, 0.00069; cyclohexanecetic (hexahydrophenylacetic) acid, 0.00236; 1-methylcyclohexane-3-acetic acid, 0.00159; cyclohexanepropionic ( $\beta$ -hexahydrophenylpropionic) acid, 0.00134. It will be seen that a methyl group in the ortho-position increases the constant of hexahydrobenzoic acid to 1.5 times its value for the *trans*-acid and to 1.25 times in the case of the *cis*-acid, which is hence the weaker of the two; similar results were obtained by Smith (Abstr., 1898, ii, 284) with the *cis*- and *trans*-modifications of hexahydrophthalic and hexahydroterephthalic acids. In the case of maleic, fumaric, crotonic, and isocrotonic acids, however, Ostwald (Abstr., 1889, 818) found that the *cis*-forms have constants much greater than those of the corresponding *trans*-isomerides. A methyl group in the para-position lowers the dissociation constant in the ratio 1.2:1, whilst in the meta-position it is practically without influence.

Comparison of the above numbers with the values of  $K$  for benzoic (0.00600) and *o*- (0.0120), *m*- (0.00514), and *p*-toluic (0.00515) acids shows that the presence of the extra six hydrogen atoms in the hexahydrogenated acids weakens the corresponding aromatic acids to extents varying from 3.3 to 5.8 times. The hexahydrogenation of phenylacetic acid lowers its constant only 2.3 times, whilst with  $\beta$ -hexahydrophenylpropionic acid the weakening influence of the six hydrogen atoms and the strengthening action of the phenyl group compensate one another, so that the acid has the same constant as propionic acid. The weakening action of a methyl group in the meta-position is shown by the constant of 1-methylcyclohexane-3-acetic acid.

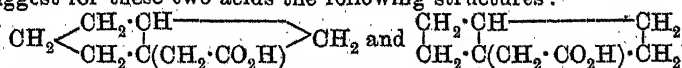
The value of  $K$  for the *trans*-form of 3:5-dimethylcyclohexane-carboxylic acid is 0.00109, and for the corresponding *cis*-modification, 0.00107. The insertion of two methyl groups in the meta-positions hence lowers the constant of cyclohexanecarboxylic acid in the ratio 1.25:1, although one such group is almost without influence.

A methyl group attached to the same carbon atom as the carboxyl group causes considerable lowering in the constant, which for 1:3-dimethylcyclohexanecarboxylic acid has the value 0.000630.

cyclo- $\Delta^1$ -Hexeneacetic acid,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , has the constant 0.00249, and the isomeric acid,



the constant 0.00260. Since unsaturated acids in general have high dissociation constants, whilst the above numbers are about the same as the value (0.00236) found for hexahydrophenylacetic acid, the authors suggest for these two acids the following structures:



The value of  $K$  for cyclopropanecarboxylic acid is 0.00150; cyclobutanecarboxylic acid, 0.00180; cyclopentanecarboxylic acid, 0.00124;

3-methylcyclopentanecarboxylic acid, 0.00107; 2-ethylcyclopentanecarboxylic acid, 0.00111; cycloheptanecarboxylic acid, 0.00122; vinylacetic acid, 0.00465.

In the series of non-substituted cycloaliphatic acids, the constant of an acid with an even number of carbon atoms is greater than the constants of the two neighbouring acids with odd numbers of carbon atoms.

T. H. P.

**Quantitative Estimation of the Products of Nitration of *m*-Chloro- and *m*-Bromo-benzoic Acid.** ARNOLD F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 260—266).—The composition of the product obtained on nitrating *m*-chloro- or *m*-bromo-benzoic acid has again been determined, because the results previously obtained by two different methods did not agree very closely (compare Abstr., 1900, i, 638; 1901, i, 591). The method adopted in this investigation was to extract the nitration product with water, care being taken to keep the solution saturated with 3-chloro- or 3-bromo-2-nitrobenzoic acid, and to titrate the solution so obtained with standard alkali. It was found that the product formed by nitrating *m*-chlorobenzoic acid at 0° and -30° contained 92 and 93% of 3-chloro-6-nitrobenzoic acid and 8 and 7% of 3-chloro-2-nitrobenzoic acid respectively. The corresponding bromobenzoic acid gave under similar conditions 87 and 89% of 3-bromo-6-nitrobenzoic acid and 13 and 11% of 3-bromo-2-nitrobenzoic acid respectively.

W. H. G.

***o*-Bromophenyl- and  $\alpha$ -Bromophenyl-acetamide.** JOAN POPOVICI (*Ber.*, 1908, 41, 4052).—In reply to Steinkopf and Benedek (Abstr., 1908, i, 981), it is pointed out that *o*-bromophenylacetamide (m. p. 186—187°) has been prepared previously (*Diss.*, 1906) by the hydrolysis of *o*-bromobenzyl cyanide.

J. J. S.

**Desylanthranilic Acid.** ROMUALD WECKOWICZ (*Ber.*, 1908, 41, 4144—4147).—*Desylanthranilic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CHPh}\cdot\text{COPh}$ , m. p. 231—232°, is obtained by heating equal molecular quantities of anthranilic acid and benzoin. The *silver, calcium, barium, magnesium, and zinc* salts are mentioned. The *acetyl* derivative,  $\text{C}_{23}\text{H}_{19}\text{O}_4\text{N}$ , has m. p. 198—200°, and the *oxime*,  $\text{C}_{21}\text{H}_{18}\text{O}_3\text{N}_2$ , has m. p. 185—186°. By nitration by concentrated sulphuric and nitric acids, a *tetranitro-desylanthranilic acid*,  $\text{C}_{21}\text{H}_{18}\text{O}_{11}\text{N}_5$ , is obtained, which sinters and darkens at 85°, and decomposes at 105—130°. Desylanthranilic acid and phenylhydrazine react in acetic acid to form a yellow, crystalline substance,  $\text{C}_{33}\text{H}_{27}\text{N}_5$ , m. p. 229—230°, which is insoluble in alkalis or dilute acids.

C. S.

**Intramolecular Rearrangement of Phthalamic Acids. III.** J. BISHOP TINGLE and H. F. ROLKER (*J. Amer. Chem. Soc.*, 1908, 30, 1882—1894).—In earlier papers (Abstr., 1907, i, 692, 1044), it has been shown that phthalanil is formed by the action of aniline on phthalanilic acid at a comparatively low temperature. A study has now been made of the action of pyridine, quinoline, ethylaniline, diphenylamine, aniline,  $\alpha$ - and  $\beta$ -naphthylamine, and

benzylamine on phthalanilic, *o*-, *m*-, and *p*-tolylphthalamic, *m*- and *p*-nitrophenylphthalamic, and  $\alpha$ - and  $\beta$ -naphthylphthalamic acids.

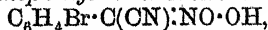
Pyridine and quinoline reacted with all these acids with formation of the corresponding phthalimide. Ethylaniline also gave the phthalimides, except in the case of  $\beta$ -naphthylphthalamic acid, which failed to react under the conditions of the experiment. Diphenylamine did not effect any change. Aniline gave phthalanil with each of the acids; it also yielded some phthalanilic acid with the three tolylphthalamic acids, and some *phenyl-p-tolylphthalamide*, m. p. 168°, with the *p*-tolyl derivative.  $\alpha$ -Naphthylamine failed to produce any change with the  $\alpha$ - and  $\beta$ -naphthyl- and *p*-nitrophenyl-phthalamic acids, but with the other compounds it gave  $\alpha$ -naphthylphthalamic acid, mixed in two cases with *m*- and *p*-tolylphthalimide respectively. A comparison of these results with those produced by aniline shows that the phenyl and naphthyl groups are mutually replaceable in the system  $R \cdot NH_2 \rightleftharpoons R' \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$ . The velocity appears to be greatest when R is  $C_{10}H_7$ .  $\beta$ -Naphthylamine reacted in a similar manner to  $\alpha$ -naphthylamine. *o*-, *m*-, and *p*-Toluidine were each treated only with the particular phthalamic acid yielded by the individual amine, and the product consisted of *o*-, *m*-, and *p*-tolylphthalimide respectively. The efficiency of these amines in producing the imide is less than that of quinoline, pyridine, and ethylaniline. *m*- and *p*-Nitroanilines failed to react with *m*- and *p*-nitrophenylphthalamic acids respectively. Benzylamine formed salts with *m*-tolyl-, *m*-nitrophenyl-, and  $\alpha$ - and  $\beta$ -naphthyl-phthalamic acids; in the case of the *m*-nitrophenyl and  $\alpha$ -naphthyl compounds some dibenzylphthalamide was produced.

These results show that the change of the phthalamic acids into phthalimides,  $R \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H \rightarrow C_6H_4 \cdot \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} NR$ , depends on (1) the nature of R, the stability of the acid increasing as R becomes more negative; (2) the temperature, increase of temperature facilitating the transformation; (3) the nature of the amine, the activity being greater the more positive the amine; and (4) the nature of the solvent. Alcohol (95%) is very active in favouring the transformation, and it is suggested that this is due to salt-formation.

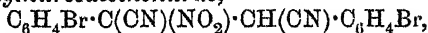
The following compounds are described: *m*-Tolylphthalamic acid, m. p. 159–161°, needles or plates. *p*-Tolylphthalamic acid, m. p. 160°, white, lustrous flakes. *m*-Nitrophenylphthalamic acid, m. p. 202°, and the corresponding *p*-derivative, m. p. 186°. *m*-Tolylphthalimide has m. p. 170–172°. Benzylamine *m*-tolylphthalamate and quinoline and benzylamine *m*-nitrophenylphthalamates are also described. E. G.

**Condensation of Ethyl Nitrate and *p*-Bromobenzyl Cyanide.** WILHELM WISLICENUS and HEINRICH ELVERT (*Ber.*, 1908, 41, 4121–4133. Compare *Abstr.*, 1905, i, 284).—The reaction between ethyl nitrate, *p*-bromobenzyl cyanide, and sodium ethoxide in alcohol-etheral solution yields sodium *p*-bromophenylisonitroacetone nitrile,  $C_6H_4Br \cdot C(OH) : NO \cdot ONa$ , which crystallises in colourless leaflets and decomposes above 300°

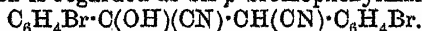
The *potassium* salt, which darkens at  $200^{\circ}$  and has m. p.  $254-256^{\circ}$  (decomp.), is obtained in better yield by using potassium ethoxide; the *copper*, *barium*, and *silver* salts are described. From a 5% aqueous solution of the sodium salt and dilute sulphuric acid in a freezing mixture, *p*-bromophenylisonitroacetoneitrile,



m. p.  $64^{\circ}$  (decomp.), is obtained, which is less unstable than the compounds described previously (*loc. cit.*). By spontaneous decomposition, it yields water and oxides of nitrogen, together with one or more of three other substances,  $\alpha\beta$ -bis-*p*-bromophenyl- $\alpha$ -nitrosuccinonitrile,  $\alpha\beta$ -bis-*p*-bromophenylmaleonitrile (*pp'*-dibromo-*aa'*-dicyanostilbene), and *p*-bromobenzoic acid, according to the temperature. *Bis*-*p*-bromophenylnitrosuccinonitrile,



m. p.  $130-134^{\circ}$ , obtained together with dibromodicyanostilbene by the slow decomposition of *p*-bromophenylisonitroacetoneitrile at a low temperature, or by warming the benzene solution of the precipitate obtained by acidifying the aqueous solution of the sodium salt with dilute sulphuric acid, separates from alcohol in colourless needles, and develops a purplish-red colour with phenol and concentrated sulphuric acid. When heated above its m. p., it loses 1 mol.  $\text{HNO}_3$ , and forms the second of the three substances mentioned above, whilst by repeated crystallisation from alcohol it is changed into a *substance*, m. p.  $162^{\circ}$ , which is regarded as bis-*p*-bromophenylmalonitrile,



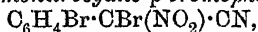
*pp'*-Dibromo-*aa'*-dicyanostilbene,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{CN})\cdot\text{C}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Br}$ , m. p.  $214-215^{\circ}$ , is obtained by warming a benzene or ethereal solution of *p*-bromophenylisonitroacetoneitrile until the evolution of nitric oxide ceases, and quantitatively by treating the sodium salt with dilute sulphuric acid at the ordinary temperature; it separates from benzene in colourless prisms, and is hydrolysed by 10% alcoholic potassium hydroxide, giving a product which by acidification yields bis-*p*-bromophenylmaleic anhydride, m. p.  $208-210^{\circ}$ , and a little *p*-bromobenzoic acid. When an acidified solution of sodium *p*-bromophenylisonitroacetoneitrile is distilled with steam, the chief product of the decomposition is *p*-bromobenzoic acid.

When sodium *p*-bromophenylisonitroacetoneitrile and excess of sodium nitrite in aqueous solution are slowly treated with dilute sulphuric acid at  $0^{\circ}$ , *p*-bromoisnitrosobenzyl cyanide is obtained, which is hydrolysed by dilute sodium hydroxide, yielding *p*-bromophenylloximinooacetic acid,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{NOH})\cdot\text{CO}_2\text{H}$ , m. p.  $160-161^{\circ}$ . Methyl iodide reacts with an alcoholic solution of sodium *p*-bromophenylisonitroacetoneitrile at  $100^{\circ}$  to form *p*-bromo-oximinobenzyl cyanide, and with the silver salt at the ordinary temperature, yielding the methyl ether,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{CN})\cdot\text{NO}\cdot\text{OMe}$ , m. p.  $110^{\circ}$ .

Boiling dilute sodium hydroxide converts sodium *p*-bromophenylisonitroacetoneitrile into sodium *p*-bromophenylisonitromethane, from which Hantzsch and Schultze's *p*-bromophenylisonitromethane (Abstr., 1896, i, 672) is obtained by acidification; at  $150-160^{\circ}$  the action of the alkali hydroxide results in the formation of *pp'*-dibromostilbene,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\text{Br}$ , m. p.  $208-210^{\circ}$ , which forms a *dibromide*,

$C_{14}H_{10}Br_4$ , m. p. 235—240° (decomp.). Reduction of sodium *p*-bromophenylisnitroacetoneitrile by zinc and sodium hydroxide yields *amino-p-bromophenylacetic acid*,  $C_6H_4Br \cdot CH(NH_2) \cdot CO_2H$ , which crystallises in colourless leaflets, sublimes at 265°, and is soluble in dilute acids or alkalis.

Bromine acts on a cold solution of sodium *p*-bromophenylisnitroacetoneitrile to form *bromonitrocyano-p-bromophenylmethane*,

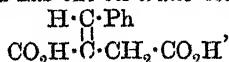


which is unstable, and by warming yields *p*-bromobenzoyl cyanide,  $C_6H_4Br \cdot CO \cdot CN$ , m. p. 65—66°, from which phenylhydrazine in ether produces *p-bromobenzoylphenylhydrazine*,  $C_6H_4Br \cdot CO \cdot N_2H_5Ph$ , m. p. 198—200°, which gives the Bülow reaction. The hydrolysis of *p*-bromobenzoyl cyanide by concentrated hydrochloric acid yields *p-bromobenzoylformamide*,  $C_6H_4Br \cdot CO \cdot CO \cdot NH_2$ , m. p. 128—129°, which is converted by boiling water containing a little sodium hydroxide into *p-bromobenzoylformic acid*,  $C_6H_4Br \cdot CO \cdot CO_2H$ , m. p. 108°, which responds to Claisen's test for benzoylformic acid.

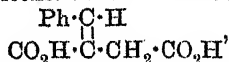
C. S.

**Indoneacetic Acids. IV. Configuration of Phenylitaconic and Phenylaticonic Acids.** HANS STOBBE and OTTO HORN (*Ber.*, 1908, 41, 3983—3988. Compare *Abstr.*, 1902, i, 542; 1904, i, 503; 1906, i, 361).—The method of determining the configuration of stereoisomeric substituted itaconic acids by cold concentrated sulphuric acid, whereby the *cis-trans*-modification merely anhydrides, whilst the *cis*-isomeride “indonises,” has been applied to  $\gamma$ -phenylitaconic and  $\gamma$ -phenylaticonic acids, which Fittig has shown to be stereoisomerides (*Abstr.*, 1904, i, 418).

$\gamma$ -Phenylitaconic acid has the *cis-trans*-configuration



since it is converted by sulphuric acid at 0° into the *anhydride*, m. p. 164°.  $\gamma$ -Phenylaticonic acid is the *cis*-modification,



since with 99% sulphuric acid at -12° it yields the three following indone derivatives. 1-*Indone-2-acetic acid*,  $C_6H_4 \begin{array}{c} <CH \\ >CO \end{array} \cdot CH_2 \cdot CO_2H$ ,

m. p. 99°, crystallises in yellow needles or prisms, and forms a yellow *semicarbazone*, m. p. 199° (decomp.). The *lactone* of 3-hydroxy-1-

hydrindone-2-acetic acid,  $C_6H_4 \cdot \begin{array}{c} CH \cdot O \\ CO - CH \cdot CH_2 \end{array} > CO$ , m. p. 123°, forms

colourless needles, and yields with 10% sodium hydroxide the golden-yellow sodium salt of 1-indone-2-acetic acid. Bimolecular 1-*indone-2-acetic acid*,  $C_{22}H_{16}O_6$ , m. p. 229°, is colourless, and gives a colourless solution with 10% sodium hydroxide, which turns bluish-violet and finally brown by warming; the cooled solution on acidification gives a substance, m. p. 135° (decomp.). Formulae are suggested for the bimolecular acid, in which the absence of colour indicates that fewer chromophores are present than in the yellow unimolecular acid.

C. S.

**Electrolysis of Santonin and of its Derivatives.** ERNESTO PANNAIN (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 499—500).—The electrolysis of santonin in aqueous acetic acid solution yields santonone, the carbonyl group of the santonin being reduced, and two molecules condensed with elimination of water. Under similar conditions, benzophenone yields benzopinacone. The experiments are being extended to various santonin derivatives, and to artemesin, camphor, purine derivatives, etc.

T. H. P.

**Equilibria among the Stereoisomerides of Santonin.** MARIO LEVI-MALVANO and ANTONIO MANNINO (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 484—494).—The authors have prepared melting-point curves for the following pairs of santonin derivatives.

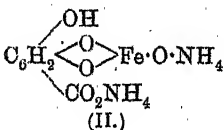
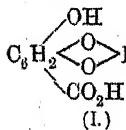
*iso*- and *l*-Acetyldesmotroposantonin: the curve here consists of three branches with two eutectic points, thus confirming the existence of racemic acetyldesmotroposantonin. The reciprocal solubilities of the racemic form in the two active forms are practically equal. Theoretically, the compound with the lower melting point, in this case the racemic modification, should be the more soluble, and this phenomenon, which is general in a binary system, has been verified in several instances where the difference between the melting points is greater than in the present case.

Acetyldesmotroposantonin and acetyl-*l*-desmotroposantonin: in this case the two stereoisomerides give only mixtures, the solubility curve of acetyldesmotroposantonin consisting of two branches, the first of which resembles a solid solution curve.

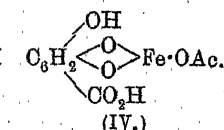
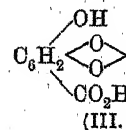
Acetyldesmotroposantonin and acetyl-*isodesmotroposantonin* yield only mixtures, as also do desmotroposantonous and *isodesmotroposantonous* acids.

T. H. P.

**Complex Salts of Gallic Acid. Ferrigallic Inks.** I. SILBERMANN and H. OZOROVITZ (*Chem. Zentr.*, 1908, ii, 1024—1025; from *Bul. Soc. Sci. Bucuresti*, 1908, 17, 43—57).—Aqueous solutions of gallic acid yield a blue precipitate with ferric chloride which is probably *chloroferrigallic acid* (I); it dissociates readily into gallic acid and ferric chloride



when treated with acid, when warmed, or when kept for some time.



The addition of ammonia or alkalis to chloroferrigallic acid produces a precipitate which is soluble in excess of the precipitant, giving an intensely reddish-yellow solution. The compound with ammonia,

ammonium ammonoxyferrigalate (II), is obtained by precipitating with alcohol; it forms a shining black, brittle mass containing  $4\text{H}_2\text{O}$ , and is very soluble in cold water, giving an intense violet-blue solution. Ammonia turns this solution somewhat red; alkalis, brownish-yellow; and acetic acid produces a dark blue coloration.

Alcohol added to the dissociated yellow solution of chloroferrigallic acid causes the precipitation of *hydroxyferrigallic acid* (III), a blue, flocculent substance. It appears to be the intermediate compound between (I) and (II), and may also be prepared by shaking freshly precipitated ferric hydroxide with a solution of gallic acid. The blue solution obtained from substance (II) with acetic acid contains acetylferri-gallic acid (IV), and by heating this solution, hydroxyferri-gallic acid is precipitated, which is converted into soluble chloro- or acetyl-ferri-gallic acid when treated with hydrogen chloride or acetic acid respectively. A neutral ammonium gallate solution when shaken with ferric hydroxide yields the deep red, sparingly soluble ammonium hydroxyferrigallate, which, in presence of hydrogen chloride, gives the insoluble blue acid (III), and with ammonia the neutral, soluble salt (II).

Compounds having two or more hydroxyl groups, or one hydroxyl and one carboxyl group, in the ortho-position give similar complex iron ammonium salts, which are soluble in water with a more or less blood-red colour, and are precipitated by alcohol from such solutions.

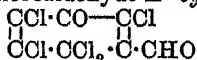
The complex iron ammonium salt of tannin is slightly soluble in water, insoluble in 10–15% alcohol; catechol and pyrogallol give a blood-red-coloured solution, from which alcohol causes a reddish-violet precipitate to separate.

Methylenedigallic acid yields a blood-red salt which is soluble in water, alcohol precipitating it in the form of a greyish-black powder. Salicylic acid gives a less intense orange-red solution, from which alcohol causes a red substance to separate.

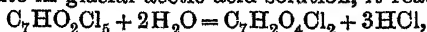
Besides ammonia and alkali hydroxides, complex salts are obtained with alkali carbonates and other salts of alkaline reaction, also alkaline earth hydroxides and organic bases. Aniline gives with gallic acid, and ferric chloride a sparingly soluble salt, which resembles in colour those of the alkali salts rather than the ammonium salt. Further, it is found that ferrous salts behave in a similar manner to ferric salts; for instance, ferrous sulphate with gallic acid and ammonia gives a deep red solution, from which alcohol causes precipitation.

Nearly every salt of a multivalent metal is capable of forming complex salts with gallic acid and alkali. J. V. E.

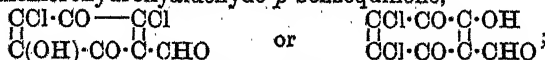
Pentachloro- and Heptachloro-*m*-hydroxybenzaldehyde. THEODOR ZINCKE and W. BROEG (*Annalen*, 1908, 363, 221–245).—The authors have investigated the properties of aldehydotrichloro-quinodichloride [pentachloroaldehydo- $\Delta^2$ -cyclohexadienone],



(Biltz and Kammann, *Abstr.*, 1902, i, 162); its aldehydic nature is confirmed by the formation of a methylal and a diacetate. With potassium acetate in glacial acetic acid solution, it reacts thus:



forming dichlorohydroxyaldehydo-*p*-benzoquinone,



this with sulphurous acid yields a trihydroxy-derivative, which with acetic anhydride gives a penta-acetyl derivative, and with aniline it forms a compound,  $\text{OH} \cdot \text{C}_6\text{O}_2\text{Cl}(\text{NHPh}) \cdot \text{OH} : \text{NPh}$ .

On chlorination, the above pentachloro-compound gives heptachloro-aldehydo- $\Delta^2$ -cyclohexen-1-one,  $\begin{array}{c} \text{CCl} \cdot \text{CO} \cdot \text{CCl}_2 \\ | \quad | \\ \text{CCl} \cdot \text{CCl}_2 \cdot \text{CCl} \cdot \text{CHO} \end{array}$ , which on reduction furnishes tetrachloro-*m*-hydroxybenzaldehyde; with sodium hydrogen sulphite, pentachlorophenol, and with concentrated sulphuric acid in glacial acetic acid solution, tetrachloro-*p*-benzoquinone. The heptachloro-compound on heating yields the compound  $\text{C}_{12}\text{O}_2\text{Cl}_8$  (Zincke and Schaum, *loc. cit.*), m. p.  $320^\circ$ .

The *dimethyl* ether of pentachloroaldehyde- $\Delta^2$ -cyclohexadienone,  $\text{C}_9\text{H}_7\text{O}_8\text{Cl}_5$ , forms small, colourless needles, m. p.  $108^\circ$ . The corresponding *diacetyl* compound crystallises in small, white needles, m. p.  $186$ — $187^\circ$ . 2:6-Dichloro-5-hydroxy-3-aldehyde-*p*-benzoquinone forms glistening, yellow leaflets, m. p.  $197$ — $198^\circ$  (decomp.), which, under the influence of light, rapidly turn copper-red and finally greyish-green. The *potassium* salt forms small, dark red needles. The *dianilide*,  $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}$ , forms orange-red crystals, m. p.  $250^\circ$ . 2:4-Dichloro-3:5:6-trihydroxybenzaldehyde, prepared by reducing the hydroxyquinone with sulphurous acid, forms small, yellow crystals, m. p.  $192^\circ$ ; the *penta-acetyl* derivative crystallises in small, white needles, m. p.  $143^\circ$ . On warming the hydroxyquinone with dilute *potassium* hydroxide, 6-chloro-2:5-dihydroxy-3-aldehyde-*p*-benzoquinone,  $\text{C}_7\text{H}_5\text{O}_5\text{Cl}$ , is obtained; it forms small, brown crystals sintering at  $195^\circ$ ; the *potassium* and *sodium* salts form red needles.

Heptachloroaldehyde- $\Delta^2$ -cyclohexen-1-one forms glistening crystals containing  $1\frac{1}{2}\text{H}_2\text{O}$ , m. p.  $107$ — $112^\circ$  (evolving water); with alcohol and sulphuric acid it yields the *ethyl* ether,  $\begin{array}{c} \text{CCl} \cdot \text{CO} \cdot \text{CCl}_2 \\ | \quad | \\ \text{CCl} \cdot \text{CCl}_2 \cdot \text{CCl} \cdot \text{CH}(\text{OH}) \cdot \text{OEt} \end{array}$ , colourless needles, m. p.  $110$ — $111^\circ$  (losing alcohol), the *acetyl* derivative of which forms white needles, m. p.  $92^\circ$ , and with acetic anhydride and sulphuric acid it gives the *diacetyl* derivative,

$\begin{array}{c} \text{CCl} \cdot \text{CO} \cdot \text{CCl}_2 \\ | \quad | \\ \text{CCl} \cdot \text{CCl}_2 \cdot \text{CCl} \cdot \text{CH}(\text{OAc})_2 \end{array}$ , white leaves, m. p.  $171^\circ$ . With methyl alcohol in presence of sodium methoxide the heptachloro-compound yields an *additive* compound,

$\begin{array}{c} \text{CCl} \cdot \text{C}(\text{OH})(\text{OMe}) \cdot \text{CCl}_2 \\ | \quad | \\ \text{CCl} \cdot \text{CCl}_2 \text{ ————— } \text{CCl} \cdot \text{CHO} \end{array}$ , transparent leaflets, m. p.  $98$ — $100^\circ$ , which with excess of sodium methoxide furnishes the tetramethoxy-compound, probably:

$\begin{array}{c} \text{CCl} \cdot \text{C}(\text{OH})(\text{OMe}) \cdot \text{C} \cdot \text{OMe} \\ | \quad | \\ \text{CCl} \cdot \text{C}(\text{OMe})_2 \text{ ————— } \text{CCl} \end{array}$ , m. p.  $150$ — $152^\circ$  (Zincke and Schaum, *Abstr.*, 1894, i, 232, give  $142$ — $143^\circ$ ); the *silver* salt is a yellowish-white, amorphous powder.

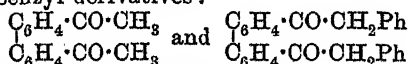
J. C. C.

**Phenanthrene Series. XXV. Phenanthrene Derivatives from 9:9-Dichloro-10-phenanthrene.** JULIUS SCHMIDT and HERMANN LUMPP (*Ber.*, 1908, 41, 4215—4225).—The authors have investigated the reactions of 9:9-dichloro-10-phenanthrene; the substance is best prepared by the action of phosphorus pentachloride on phenanthraquinone (Lachowicz, *Abstr.*, 1883, 666; 1884, 82), but

it is also formed by treating phenanthraquinone with chlorine in presence of red phosphorus. It crystallises in yellowish-white prisms, m. p. 168—169°. 9-Chloro-10-hydroxyphenanthrene is best prepared by treating the preceding compound with tin and hydrochloric acid; it forms white prisms, m. p. 121° (Lachowicz gives 122—123°); the *picrate*, cinnabar-red prisms, m. p. 169—170°, *acetate*, yellow prisms, m. p. 145—147°, and *benzoate*, pale yellow prisms, m. p. 165—166°, are described. On reduction with zinc dust and glacial acetic acid, chlorohydroxyphenanthrene yields 10-hydroxyphenanthrene, and when heated with aqueous ammonia it gives di-9-hydroxyphenanthryl-10-amine (Schmidt and Kämpf, Abstr., 1902, i, 757), which has m. p. 230° (decomp.), and not 168—170° as previously given. This substance exhibits phototropism in ethereal solution. When boiled with acetic anhydride it furnishes phenanthroxazine (Bamberger and Grob, Abstr., 1901, i, 280). Chlorohydroxyphenanthrene, on sulphonation, gives rise to a *disulphonic acid*, which forms glistening, dark brown leaflets containing  $10\text{H}_2\text{O}$ ; the *barium* salt crystallises in dark green leaflets with  $4\frac{1}{2}\text{H}_2\text{O}$ . 3-Nitrophenanthraquinone is obtained in a 30% yield by boiling chlorohydroxyphenanthrene with nitric acid, D 1.35; this is an important improvement on the previous methods of preparation (Abstr., 1908, i, 995), and it is hoped to employ this substance for the synthesis of further scission products of the opium alkaloids.

J. C. C.

**Diacetophenone, Dideoxybenzoin, and Dibenzil.** THEODOR ZINCKE and W. TROPP (*Annalen*, 1908, 363, 302—312).—The authors have previously shown (Abstr., 1908, i, 786) that the ditertiary alcohols prepared from phenanthraquinone by the aid of organo-magnesium compounds are oxidised by chromic acid to diketones; the reactions of the methyl and benzyl derivatives:



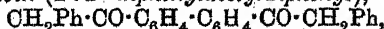
have now been further investigated.

*oo'*-Diacetophenone (2 : 2'-diacetyldiphenyl),  $\text{C}_6\text{H}_4\text{Ac}\cdot\text{C}_6\text{H}_4\text{Ac}$ , prepared by oxidising a glacial acetic acid solution of dihydroxydimethyl-

dihydrophenanthrene,  $\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{OH}$   
 $\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{OH}$ , with chromic acid, crystallises in

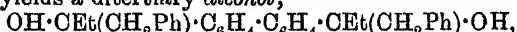
small, glistening leaflets or colourless prisms, m. p. 84°; the *dioxime*,  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$ , crystallises in compact, colourless needles, m. p. 212° (decomp.); the *bisphenylhydrazone*,  $\text{C}_{28}\text{H}_{26}\text{N}_4$ , forms large, pale yellow crystals, m. p. 178°. By the action of magnesium ethyl bromide, the ketone yields a ditertiary alcohol,  $\text{OH}\cdot\text{CMeEt}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CMeEt}\cdot\text{OH}$ , crystallising in colourless prisms, m. p. 119—120°, and on reduction with zinc dust and hydrochloric acid the parent compound is regenerated.

*oo'*-Dideoxybenzoin (2 : 2'-diphenylacetyldiphenyl),

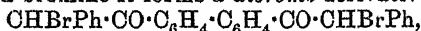


prepared by oxidising dihydroxydibenzyl-dihydrophenanthrene with chromic acid, crystallises in glistening leaflets, m. p. 139°—140°; the *dioxime*,  $\text{C}_{28}\text{H}_{24}\text{O}_2\text{N}_2$ , forms colourless needles, m. p. 108—111°; the *bisphenylhydrazone*,  $\text{C}_{40}\text{H}_{34}\text{N}_4$ , crystallises in pale yellow, glistening

leaflets, m. p. 188—189°. By the action of magnesium ethyl bromide, the ketone yields a ditertiary *alcohol*,



crystallising in colourless tablets, m. p. 130—131°; the *acetate* forms colourless leaflets, m. p. 126—128°. Dideoxybenzoin is readily reduced by zinc dust in acid or alkaline solution to the parent compound; with bromine it forms a *dibromo-derivative*,



white leaflets, m. p. 195° (decomp.), and with phosphorus pentachloride the corresponding *dichloro-derivative* is obtained in white leaflets, m. p. 196—200° (decomp.).

*isoNitrosodideoxybenzoin*,  $\text{OH} \cdot \text{N} : \text{CPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CPh} \cdot \text{N} \cdot \text{OH}$ , prepared by adding amyl nitrite to an alcoholic solution of dideoxybenzoin, crystallises in stellate clusters of white needles, m. p. 196°; it forms a pale yellow *sodium salt*. When an acetic acid solution of the *isonitroso-compound* is warmed with dilute hydrochloric acid, there is formed *oo-dibenzil*,  $\text{COPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{COPh}$ , which crystallises in sulphur-yellow, rhombic tablets and columns, m. p. 120°; it condenses with 2 mols. of *o*-phenylenediamine to a *diquinoxaline*,  $\text{C}_6\text{H}_4 \cdot \text{N} \gg \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{C} \ll \text{N} - \text{C}_6\text{H}_4$ , m. p. above 300°. J. C. C.

**Quinonoid Derivatives of Diphenyl.** I. WILHELM SCHLENK [with ANGELO KNORR] (*Annalen*, 1908, 363, 313—339).—The object of this investigation was to prepare the diphenyl analogues of *p*-benzoquinone-di-imine, -chloroimine, and -dichlorodi-imine. It has been found possible to isolate the chloroimine and dichlorodi-imine of diphenoquinone; all attempts to prepare the corresponding imines by gentle reduction of these chloroimines have, up to the present, been unsuccessful (compare Willstätter and Kalb, *Abstr.*, 1905, i, 361; 1906, i, 996).

It has long been known that coloured, complex compounds are formed when benzidine is treated with various oxidising agents (compare Zinin, *J. pr. Chem.*, 1845, 36, 98; Claus and Risler, *Abstr.*, 1881, 605; Lauth, *Abstr.*, 1891, 457; Willstätter and Kalb, *loc. cit.*; Barsilowsky, *Abstr.*, 1905, i, 549; Moir, *Trans.*, 1907, 91, 1305; *Proc.*, 1906, 22, 258). It is now shown that these substances are *meriquinonedii-immonium salts*. The behaviour of some of these salts when dissolved in water or alcohol supports the view recently put forward by Kehrman with reference to the constitution of these compounds (compare *Abstr.*, 1908, i, 699); thus *meridiphenoquinone-tetramethyldi-immonium chloride* (compare Lauth, *loc. cit.*) is not dissociated to any marked degree in aqueous solution, whilst *meriditoluquinonedii-immonium chloride* is partly, and *meridichloroditoluquinonedii-immonium chloride* is completely, dissociated in dilute alcoholic solution.

A general method for preparing halogen derivatives of benzidine and the toluidines is described, namely, treating the diamine, suspended in concentrated hydrochloric or hydrobromic acid, with chlorine or bromine respectively; the halogen enters the positions ortho to the

amino-groups; consequently, *p*- and *m*-tolidine yield tetrahalogenated derivatives, whilst only dihalogenated compounds are derived from *o*-tolidine.

The compound first obtained by Claus and Risler (*loc. cit.*) by the action of sodium hypochlorite on an aqueous solution of benzidine containing hydrochloric acid is shown to be *diphenokinonedichlorodi-imine*,

$\text{ClN}:\text{C}_6\text{H}_4=\text{C}_6\text{H}_4:\text{NCl}$ ; it is a dark reddish-brown, amorphous

powder, and, when heated rapidly, explodes slightly at about  $135^\circ$ ; it also forms microscopic, red needles, which explode at  $155\text{--}160^\circ$ . It is decomposed with explosive violence by concentrated sulphuric or nitric acid, and is reduced by stannous chloride to benzidine. *Titoloquinonedichlorodi-imine*,  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{Cl}_2$ , prepared in a similar manner from *o*-tolidine, crystallises in tufts of ruby-red needles, which explode slightly at about  $163^\circ$ . *p*-*Diphenokinonechloroimine*,  $\text{O}:\text{C}_6\text{H}_4:\text{C}_6\text{H}_4:\text{NCl}$ , prepared from 4-amino-4'-hydroxydiphenyl, is an olive-brown powder, which rapidly decomposes, forming a black, humous mass.

3:3'-*Dichloro-o-tolidine*,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{Cl}_2$ , prepared by the action of chlorine on *o*-tolidine hydrochloride suspended in concentrated hydrochloric acid, crystallises in white needles, m. p.  $160\text{--}161^\circ$ ; the *sulphate*,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{Cl}_2 \cdot 2\text{H}_2\text{SO}_4$ , forms microscopic needles. The *hydrochloride* forms white needles, m. p. about  $152^\circ$ , and is converted by ferric chloride in aqueous alcoholic solution into *meridichloroditoluquinonedi-immonium chloride*,

$(\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{MeCl} \cdot \text{C}_6\text{H}_2\text{MeCl} \cdot \text{NH}_2, \text{NH} \cdot \text{C}_6\text{H}_2\text{MeCl} \cdot \text{C}_6\text{H}_2\text{MeCl} \cdot \text{NH}),$   
 $2\text{HCl}, 2 \text{ or } 3\text{H}_2\text{O},$

obtained as a bronzy, dark blue powder; the *sulphate* forms microscopical, bronzy, dark blue needles. Similar *dibromo*-derivatives were prepared. *meriDitoluquinonedi-immonium chloride*,  $\text{C}_{28}\text{H}_{30}\text{N}_4 \cdot 2\text{HCl}$ , obtained from *o*-tolidine, is a bronzy, violet-black powder.

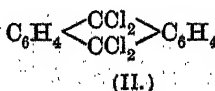
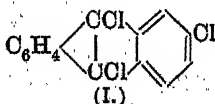
3:5:3':5'-*Tetrachlorobenzidine*,  $\text{C}_{12}\text{H}_8\text{N}_2\text{Cl}_4$ , crystallises in white, felted needles, m. p.  $226\text{--}227.5^\circ$ ; the *tetra-acetyl* derivative,

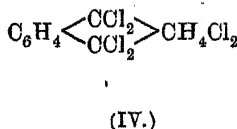
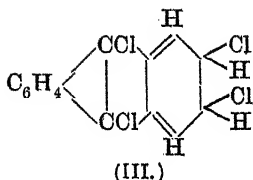
$\text{C}_{20}\text{H}_{16}\text{O}_4\text{N}_2\text{Cl}_4$ ,  
forms white needles, m. p.  $265\text{--}266^\circ$ . *Tetrabromo-m-tolidine*,

$\text{C}_{14}\text{H}_{12}\text{N}_2\text{Br}_4$ ,  
is a heavy, white, crystalline powder, m. p.  $229\text{--}230^\circ$ ; the *tetra-acetyl* derivative,  $\text{C}_{22}\text{H}_{20}\text{O}_4\text{N}_2\text{Br}_4$ , crystallises in leaflets, m. p.  $259\text{--}263^\circ$ .

W. H. G.

**Action of Phosphorus Pentachloride on Anthraquinone.**  
DAN RADULESCU (*Chem. Zentr.*, 1908, ii, 1032—1033; from *Bul. Soc. Sti. Bucuresti*, 1908, 17, 29—40).—When treated with a mixture of phosphorus pentachloride (2 mol.) and phosphorus oxychloride (4 mol.), anthraquinone yields trichloroanthracene (I), together with small quantities of isomeric dichloroanthracene dichloride ( $\alpha$  and  $\beta$ ), as well as higher chlorinated products.





The small quantity of 9:10-dichloroanthracene  $\beta$ -dichloride (III) that is found is considered to be the intermediate product between the 9:10-dichloride (II) and trichloroanthracene (I).

When anthraquinone is treated at  $175-180^\circ$  with phosphorus pentachloride (3 to  $3\frac{1}{2}$  mols.), there is produced trichloroanthracene and dichloroanthracene tetrachloride (IV), which is probably present in two stereoisomeric modifications.

9:10-Dichloroanthracene 9:10-dichloride,  $C_{14}H_8Cl_4$  (II), called the  $\alpha$ -dichloride, forms red or bluish-cream-coloured, prismatic crystals, m. p.  $139^\circ$ , at which temperature it decomposes into trichloroanthracene. When heated in a current of carbon dioxide at  $170-180^\circ$ , it gives trichloroanthracene, and when heated for a short time above the m. p., small quantities of the so-called  $\beta$ -dichloride are produced.

9:10-Dichloroanthracene 2:3-dichloride,  $C_{14}H_8Cl_4$  (III), called the  $\beta$ -dichloride, crystallises in long, greenish-yellow needles, which decompose from  $150^\circ$ , giving trichloroanthracene. It is a very unstable substance, readily losing hydrogen chloride, and when dissolved in chloroform exhibits a blue fluorescence.

Trichloroanthracene,  $C_{14}H_7Cl_3$  (I), forms dark red or pale yellow needles, m. p.  $172^\circ$ , which dissolve without decomposition in strong sulphuric acid, giving a malachite-green coloration; when warmed or kept, this colour disappears. So intense is it that a drop of an acetic acid solution of trichloroanthracene diluted 1/10,000 gives a green colour with 2 c.c. of concentrated sulphuric acid. On the addition of acetic acid, this green-coloured solution when not very dilute becomes decolorised, and develops a violet-blue fluorescence. This reaction is found to be a general one for all 9:10-halogen substituted products of anthracene.

9:10-Dichloroanthracene 2:3:9:10-tetrachloride,  $C_{14}H_8Cl_6$  (IV) (compare Schwarzer, Abstr., 1877, ii, 493), exists in two, probably stereoisomeric, modifications,  $\alpha$ , and  $\gamma$ . The  $\alpha$ -tetrachloride crystallises in silky needles, m. p.  $185^\circ$  (decomp.), with formation of trichloroanthracene.

The  $\gamma$ -tetrachloride forms transparent, strongly refracting, prismatic crystals, m. p.  $149^\circ$  (decomp.), yielding trichloroanthracene.

Schwarzer's reaction (*loc. cit.*).—When chlorine is passed into a 0.25—3.5% chloroform solution of anthracene, it is found that 9:10-dichloroanthracene is first produced, then dichloroanthracene  $\alpha$ -tetrachloride, and finally a stable compound, m. p.  $280^\circ$ , which crystallises in cream-coloured needles.

J. V. E.

Constituents of Essential Oils. Constitution of Umbellulone. FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 3988—3994).—Previous work of the author, culminating in a representation of the

constitution of umbellulone (Abstr., 1908, i, 92), has been severely criticised by Tutin (Trans., 1908, 93, 252) on the ground that the author employed impure umbellulone, from some constituent of which, other than umbellulone, homotanacetonedicarboxylic acid was produced. The author has therefore distilled 1000 grams of crude oil of *U. Californica*, and obtained a fraction, b. p. 92—94°/10 mm.,  $D^{20}_D$  0.950,  $n_D$  1.4872, and  $\alpha_D$  -37°30' (100 mm. tube). This fraction has been treated with semicarbazide hydrochloride (rather more than 2 mols.) in alcoholic solution, whereby two products have been obtained: (a) *Umbellulone semicarbazone*,  $C_{11}H_{17}ON_3$ , is almost insoluble in water, separates from methyl alcohol in snow-white crystals, decomposes at 240—243°, and yields, with the calculated quantity of dilute sulphuric acid, umbellulone, having b. p. 92.5—93°/10 mm.,  $D^{20}_D$  0.950,  $n_D$  1.48325, and  $\alpha_D$  -36°30' (100 mm. tube); (b) semicarbazido-umbellulone semicarbazone,  $C_{12}H_{24}O_2N_6$ , is soluble in hot water, and is separated completely from the solution by ammonium sulphate, decomposes above 200°, according to the rate of heating, yielding the normal semicarbazone (decomp. 240°), and by treatment with the calculated quantity of sulphuric acid yields umbellulone, having b. p. 92—94°/10 mm.,  $n_D$  1.4825, and  $\alpha_D$  -37°.

From either of these regenerated umbellulones,  $\beta$ -dihydroumbellulol,  $\beta$ -dihydroumbellulone, benzylidene- $\beta$ -dihydroumbellulone, and homotanacetonedicarboxylic acid have been prepared in succession, having properties practically identical with those described previously (*loc. cit.*); thus proving that Tutin's objections are invalid.

The author's formula for umbellulone is supported by the fact that umbellulone is converted quantitatively at 280° into thymol. C. S.

**Ethereal Oil from *Salvia sclarea*.** THOMAS F. HARVEY (*Chemist and Druggist*, 1908, 73, 393).—The author gives analyses of four samples of Dalmatian and one of Spanish oil, from which it appears that pinene, cineol, thujone, borneol, and probably camphor are the normal constituents of Dalmatian oil.

There seems to be a considerable variation in the constituents and properties of oil obtained from different sources; Dalmatian oil derived from *Salvia officinalis*, and Syrian oil from *Salvia triloba*, differ from Spanish oil obtained from a different variety of *Salvia*.

Oil from Dalmatia may be taken as typical; it has  $D$  0.915—0.930,  $\alpha_D$  +4° to +25°,  $n_D^{20}$  1.4618—1.4645; it is soluble in 1 vol. and more of 80% alcohol; acid number, 1.3—2.2; ester number, 6.7—12.6; saponification number, 6—18, and total content of borneol, 9.5—14.8.

J. V. E.

**Carbonaceous Substances and Bitumens.** K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1327—1334).—Asphalte always contains more hydrogen than coal or carbonaceous substances, and may be regarded as hydrogenated coal. This view is confirmed by a study of the products of dry distillation of asphalte. Pit coal and brown coal, on dry distillation, give highly unsaturated cyclic compounds, consisting of variously substituted benzenes and of

compounds containing less hydrogen, such as naphthalene, anthracene, chrysene, etc. With asphalt, more highly hydrogenated compounds would be expected on dry distillation, and this is found to be the case. The liquid hydrocarbons obtained in this way give, on distillation, fractions which closely resemble, in density, external appearance, and in their proportions, the fractions obtained on distilling natural naphtha. The lower fractions are remarkably stable towards the action of reagents; thus they are not appreciably attacked by sulphuric acid, nitric acid, or potassium permanganate, and they do not yield benzene nitro-derivatives when treated with a nitrating mixture. This behaviour, together with the density, points to the predominance of naphthenes in the decomposition products of asphalt. In addition, in the absence of aromatic hydrocarbons, which in naphtha may have a secondary origin, the liquid hydrocarbon fraction of asphalt differs from naphtha in the low density of the distillation residue; this is probably to be explained by the presence in naphtha of more or less asphalt, which raises the density of its residue.

The hydrogenated nature of asphalt is confirmed by the character of the distillation products, which are partly hydrogenated aromatic hydrocarbons and partly saturated hydrocarbons. The resemblance, which in some cases amounts to identity, between the decomposition products of naphtha and asphalt indicates an undoubted genetic relationship between the two substances. T. H. P.

**Chemistry of Condurango Bark.** KONRAD KUBLER (*Arch. Pharm.*, 1908, 246, 620—660. Compare Tanret, *Abstr.*, 1885, 552; Bocquillon, *J. Pharm. Chim.*, 1891, [v], 24, 485, and Carrara, *Abstr.*, 1891, 1387; 1892, 1352).—The principal constituents found in the bark, apart from dextrose and other usual components of plants, were the glucoside, condurangin, and a new polyhydric alcohol, conduritol.

Condurangin was isolated by extraction of the bark with alcohol and defecation of the alcoholic extract with acetone and chloroform. The glucoside was finally purified by fractional precipitation of its solution in alcohol with ether. Thus obtained it is an amorphous, bright yellow, slightly hygroscopic powder, soluble in water, chloroform, or alcohol, and insoluble in ether. It is bitter and optically inactive. Analyses of different preparations lead to the formula  $C_{40}H_{60}O_{10}$ . The glucoside contains two methoxyl groups. It is hydrolysed slowly in the cold, and more rapidly on heating with dilute sulphuric acid, yielding dextrose and an amorphous powder, which appears to be a mixture of at least four substances, and yields some cinnamic acid on treatment with alcoholic potassium hydroxide. Condurangin forms a clear solution with water, but this becomes opalescent or, in the case of strong solutions, gelatinous on heating, but returns to its normal condition on cooling.

*Conduritol*,  $C_6H_{10}O_4$ , m. p. 142—143°, occurs in the by-products of the purification of the crude glucoside, crystallises from hot alcohol in colourless prisms, is optically inactive, and has an intensely sweet taste. It does not reduce Fehling's solution or ammoniacal silver solution. The *tetrabenzoyl* derivative is amorphous, and the corresponding *phenylurethane*, m. p. 120°, is a colourless, tasteless powder.

Conduritol reacts in aqueous solution with bromine to form a  *dibromide*,  $C_6H_{10}O_4Br_2$ , m. p.  $196^\circ$ , and a  *monobromo-compound*,  $C_6H_{11}O_5Br$ , m. p.  $175^\circ$ . When heated with hydrochloric acid, conduritol yields, as one product, catechol. Oxidation experiments gave no results of value. It is thought that the alcohol and the monobromo-compound, referred to above, may be represented by the formulæ  $\begin{array}{c} CH \cdot CH(OH) \cdot CH \cdot OH \\ | \quad | \quad | \\ CH \cdot CH(OH) \cdot CH \cdot OH \end{array}$  and  $\begin{array}{c} CHBr \cdot CH(OH) \cdot CH \cdot OH \\ | \quad | \quad | \\ OH \cdot CH \cdot CH(OH) \cdot CH \cdot OH \end{array}$ . On steam distillation, the bark yields 0.3% of volatile oil, sp. gr. 0.9741, b. p.  $140^\circ$ ,  $[\alpha]_D + 6.724^\circ$ , having an intense, not unpleasant, aromatic odour, and consisting, in part, of higher fatty acids.

T. A. H.

**Constituents of Vincetoxicum Root.** KONRAD KUBLER (*Arch. Pharm.*, 1908, 246, 660—663).—This root has been examined in comparison with Condurango root (see preceding abstract), to which it is closely allied botanically. Vincetoxin was isolated by Tanret's method (*Abstr.*, 1885, 552), and, after purification by precipitation from its solution in chloroform by means of ether, was obtained as a colourless, amorphous powder, m. p.  $182^\circ$  (decomp.),  $[\alpha]_D - 75^\circ$  in water, having the composition  $C_{50}H_{82}O_{20}$ . On treatment with hydriodic acid, it yielded methyl iodide equivalent to 10.4% of methoxyl. On hydrolysis with dilute sulphuric acid, dextrose was formed, and a brown, amorphous substance, which did not furnish cinnamic acid when treated with alcoholic potassium hydroxide. The root also contains 3% of sucrose and some dextrose.

T. A. H.

**"Kawar" Root.** RUDOLF BOEHM and KONRAD KUBLER (*Arch. Pharm.*, 1908, 246, 663—666).—This Asclepiadaceous root, stated to be used in the Transvaal as a remedy for cancer, was examined by the method described under "Condurango" bark (see two preceding abstracts). It contained a volatile oil, choline, a sugar yielding a phenylosazone, m. p.  $215^\circ$ , and a glucoside, *kawarin*. This last is an almost colourless, amorphous powder, soluble in water or chloroform, and insoluble in ether, has m. p.  $188^\circ$  (decomp.), is optically inactive, and its aqueous solution, like that of conduragin, when heated becomes cloudy and gelatinous, but returns to its normal state on cooling. When hydrolysed with dilute sulphuric acid, the glucoside yields about 22% of a dextrorotatory, fermentable sugar, and an amorphous product, insoluble in water, which does not yield cinnamic acid when treated with potassium hydroxide in alcohol. No formula is assigned to kawarin, but it contains 58.7—59.0% of carbon, 8.37—8.53% of hydrogen, and 9.0—9.1% of methoxyl.

T. A. H.

**Quantitative Control in Chlorophyll Research.** V. BÉDLIK (*Compt. rend.*, 1908, 147, 990—993).—The control is spectrophotometric, the ratio of the coefficient of extinction to the amount of dissolved substance being regarded as increasing with the purity of

the chlorophyll preparation. The measurements are best carried out on band II ( $\lambda=615$ ) in dilute benzene solution. Band IV ( $\lambda=536$ ) is due to partial decomposition of the chlorophyll. G. B.

**1- and 2-Methylcoumarone.** JOHANNES BOES (*Chem. Zentr.*, 1908, ii, 1185; from *Apoth. Zeit.*, 1908, 23, 599).—After repeated fractionation of the distillate separated from the product of resinifying methylcoumarone by sulphuric acid, a substance is obtained having b. p. 185—198°. This gives a picrate which crystallises from alcohol in yellow needles, m. p. 79—80°, but is not a simple substance, giving when decomposed a practically colourless, pleasant-smelling oil, b. p. 189—195°, which exhibits the properties of coumarone. That a phenol and not a cresol is produced is shown by the formation of phenyl phenylcarbamate, m. p. 126°. The suggestion is made that the allylene products in coal-tar react, for the most part, with phenol, forming coumarone compounds. J. V. E.

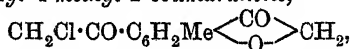
**Homologues of Coumaranone and their Derivatives.** KARL FRIES and G. FINCK (*Ber.*, 1908, 41, 4271—4284).—Stoermer's method of condensing phenoxyacetic acid by phosphoric oxide to form coumaranone gives poor yields (*Abstr.*, 1897, i, 528), and cannot therefore be used as a general method. Neither is Friedländer's method of obtaining coumaranone from ethyl coumaranonecarboxylate (*Abstr.*, 1897, i, 424) feasible. The simplest theoretical method, namely, the withdrawal of the elements of hydrogen haloid from  $\omega$ -halogen- $o$ -hydroxyacetophenones, has not been used up till now extensively, owing to the difficulty in obtaining the required acetophenones (compare Nencki, *Abstr.*, 1894, i, 85). These may be obtained easily from the chloroacetyl derivatives of the phenols.

The *chloroacetyl* derivatives of *p*-cresol, *m*-cresol, and *m*-4-xenol, obtained quantitatively by heating the phenol with chloroacetyl chloride for four hours at 135° and subsequent fractional distillation under reduced pressure, have m. p. 32°, b. p. 162°/45 mm., b. p. 153°/30 mm., and b. p. 173°/45 mm. respectively. The *anilino*-compound from the *p*-tolyl chloroacetate,  $C_6H_4Me \cdot O \cdot CO \cdot CH_2 \cdot NHPh$ , crystallises from petroleum in slightly yellow needles, m. p. 109°.

These chloroacetyl compounds, when heated with aluminium chloride, undergo isomeric change into *o*-hydroxy-derivatives; thus the chloroacetyl derivative of *p*-cresol gives *o*-chloro-2-hydroxy-5-methylacetophenone,  $OH \cdot C_6H_3Me \cdot CO \cdot CH_2Cl$ . It is obtained by heating at 140° for four hours, and then the product is distilled in steam and crystallised from petroleum; it forms long prisms, m. p. 65°; the alkaline solution becomes red, owing to chemical change. The yield is 90%; the *acetate* has m. p. 59°. *o*-Chloro-2-hydroxy-4-methylacetophenone,  $C_9H_9O_2Cl$ , obtained in a similar manner from *m*-tolyl chloroacetate in 50% yield, crystallises from petroleum in prisms, m. p. 101°, and the *o*-chloro-2-hydroxy-3:5-dimethylacetophenone,  $C_{10}H_{11}O_2Cl$ , is not obtained so easily from the isomeric chloroacetylxylenol; it separates from petroleum in needles, m. p. 92°. Interaction of chloroacetyl chloride, phenol, and aluminium chloride does not lead to such

good results as when the reaction is carried out in the two stages, as more than one chloroacetyl radicle is introduced into the nucleus; thus 3:5-dichloroacetyl-*p*-cresol (annexed formula) is obtained along with the monochloroacetyl compound by heating *p*-cresol with excess of chloroacetyl chloride and aluminium chloride; it separates from glacial acetic acid in slender needles, m. p. 168°; its acetyl derivative has m. p. 117°.

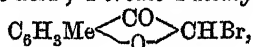
When these *o*-chloro-*o*-hydroxymethylacetophenones are heated with alcoholic sodium acetate, the corresponding methylcoumaranones are obtained; the 4-methyl-, 5-methyl-, and 4:6-dimethyl-coumaranones have m. p.'s 54°, 85°, and 75° respectively, and are slightly yellow (Stoermer and Bartsch, Abstr., 1901, i, 94, only obtained these as oils). 6-Chloroacetyl-4-methyl-2-coumaranone,



separates from glacial acetic acid in slightly yellow crystals, m. p. 173°; its alkaline solution has a blood-red colour, and is easily oxidised.

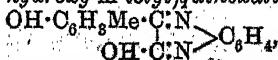
1-*p*-Nitrobenzylidene-4-methyl-2-coumaranone,  $\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}$ , obtained by the condensation of aldehyde and coumaranone in the presence of alcoholic hydrogen chloride, crystallises in yellow needles, m. p. 208°; the corresponding *o*-nitrobenzylidene compound crystallises in red needles, m. p. 156°.

These methylcoumaranones are easily brominated in an acetic acid solution of hydrochloric acid; 1-bromo-4-methyl-2-coumaranone,



forms thick, red crystals, m. p. 86°; 1-1-dibromo-4-methyl-2-coumaranone,  $\text{C}_9\text{H}_6\text{O}_2\text{Br}_2$ , forms light yellow needles, m. p. 107°, and, on treatment with lead oxide, 2-hydroxy-5-methylbenzoylformic acid is obtained. 1:1-Dichloro-4-methyl-2-coumaranone,  $\text{C}_9\text{H}_6\text{O}_2\text{Cl}_2$ , crystallises in colourless leaflets, m. p. 62°. Bromomethylcoumaranone and silver acetate, when heated in glacial acetic acid, give 1-acetoxy-4-methyl-2-coumaranone,  $\text{C}_{11}\text{H}_{10}\text{O}_4$ , which forms long, yellow prisms, m. p. 74°. Experiments designed to remove the acetyl radicle by hydrolysis have so far been without the desired result.

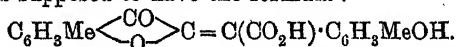
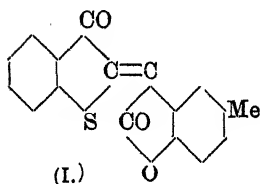
1-Oximino-4-methylcoumaranone,  $\text{C}_9\text{H}_7\text{O}_3\text{N}$ , obtained from the methylcoumaranone and nitrous acid, crystallises from methyl alcohol in yellow leaflets, m. p. 187°, and when heated at 60° with hydrochloric acid it is converted into 6-hydroxy-*m*-toluoylformic acid,  $\text{C}_9\text{H}_8\text{O}_4$ , crystallising from petroleum in almost colourless needles, m. p. 105°. This acid behaves somewhat differently from its lower homologue, as on heating the dry acid, long, yellow prisms of probably 4-methyl-diketo-coumaran,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CO}$ , are produced in impure condition (compare Schad, Abstr., 1893, i, 279). The anil of 6-hydroxy-*m*-toluoylformic acid,  $\text{C}_{15}\text{H}_{13}\text{O}_3\text{N}$ , crystallises in yellow needles, m. p. 80°. Condensation of the hydroxytoluoylformic acid with *o*-phenylenediamine yields 2-hydroxy-3-(4-hydroxy-*m*-tolyl)quinoxaline,



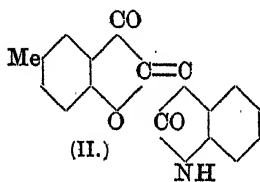
crystallising in yellow needles, m. p. at re 300°.



coumaranone], and therefore an oxygen isologue of indirubin. All the bismethylcoumaranones prepared are well-characterised, orange compounds, which sublime in a vacuum, and are stable towards cold alkalis. 1:2-Bis-5-methylcoumaranone has m. p. 279°; 4:5'-dimethyl-1:2'-biscoumaranone, m. p. 286°, and 5:4'-dimethyl-1:2'-biscoumaranone, m. p. 258°. These oxygen isologues of dimethylindirubin are quickly dissolved by alcoholic potassium hydroxide, and coloured, crystalline dipotassium salts are precipitated, hydrolysed by water, and, on acidification with acetic acid, a yellow, insoluble acid is precipitated, which is quickly reconverted into the dimethylcoumaranone; the acid is supposed to have the formula:



When hydroxythionaphthen, itself prepared by heating the carboxylic acid, is condensed with 6-hydroxy-*m*-toluoylformic acid, 1-ketothionaphthbenzyl-(2)-4-methylcoumaranone, formula I, is produced; it forms red needles, m. p. 257°, is very stable towards aqueous alkalis, and does not give a sparingly soluble salt with alcoholic potassium hydroxide. It sublimes in a vacuum, and may also be obtained by heating dibromohydroxythionaphthen and 4-methylcoumaranone in acetic acid in 60% yield.

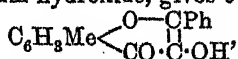


The condensation of isatin and 4-methylcoumaranone leads to the formation of (1)-4-methylcoumaranonyl-3-indole, formula II, which crystallises from glacial acetic acid in dark red needles, m. p. 286°, and contains acetic acid, which is only driven off at 200°. W. R.

**Conversion of Benzylidenecoumaranones into Flavonols.** KARL AUWERS and KARL MÜLLER (*Ber.*, 1908, 41, 4233—4241).—The authors find that when dibromobenzylidene-4-methylcoumaranone is treated with 2 mols. of potassium hydroxide in hot alcoholic solution, 6-methylflavonol is obtained.

4-Methylcoumaran-2-one is best prepared by warming an alcoholic solution of *o*-chloroacetyl-*p*-cresol with a concentrated, aqueous solution of 1.5 equivs. of sodium hydroxide. It forms long, glistening, colourless needles, m. p. 51—52° (the substance is described by Stoermer and Bartsch as an oil: *Abstr.*, 1901, i, 94). The semicarbazone has m. p. 230—232°: Stoermer (private comm.), 230°, Stoermer and Bartsch, 181°; the oxime, m. p. 144—145°: Stoermer, 144—145°, Stoermer and Bartsch, 144°; the *o*-hydroxybenzylidene compound softens at 222°, m. p. 225—226°: Stoermer, 221—222°, Stoermer and Bartsch, 210°; the *p*-hydroxybenzylidene compound, m. p. 254—255°: Stoermer, 200°, Stoermer and Bartsch, 163°. The *benzylidene* derivative forms pale yellow prisms, m. p. 119°, and, on bromination, yields

the *dibromo*-derivative,  $\text{C}_6\text{H}_5\text{Me} \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CBr} \cdot \text{CHBrPh}$ , which crystallises in compact, broad pointed prisms, m. p.  $158^\circ$  (decomp.). This, on treatment with potassium hydroxide, gives 6-methylflavanol,

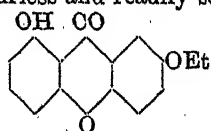


in compact, broad, pale yellow prisms, m. p.  $196-197^\circ$ ; the *benzoate* forms glistening, colourless needles, m. p.  $167-168^\circ$ . 6-Methyl-

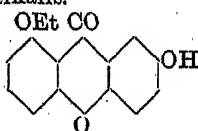
flavanone,  $\text{C}_6\text{H}_5\text{Me} \begin{smallmatrix} \text{O}-\text{CHPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$ , prepared by the action of sodium

hydroxide on a mixture of *o*-acetyl-*p*-cresol and benzaldehyde, forms colourless leaflets, m. p.  $106-107^\circ$ ; the *oxime* crystallises in small, yellow needles, m. p.  $148-149^\circ$ . By boiling with 10% sulphuric acid, the flavanone is converted into 6-methylflavanol. J. C. C.

The Two Isomeric Monoalkyl Ethers of Euxanthone. JOSEF HERZIG and K. KLIMOSCH (*Ber.*, 1908, 41, 3894-3897).—Of the two isomeric monoethyl ethers of euxanthone described by Herzig (*Abstr.*, 1891, 1349), one (I) is yellow and insoluble in alkalis, whilst the other (II) is colourless and readily soluble in alkalis.



(I.)

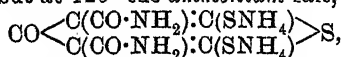


(II.)

It is now found that the colourless ether dissolves in dilute alkalis with an intense yellow colour, and a *potassium* salt has been isolated. With alkyl iodides or methyl sulphate, this gives a white dialkyl ether, and with carbon dioxide the white monoethyl ether is regenerated. The latter also gives intensely yellow solutions with acids, and the *hydrochloride* forms orange-yellow needles which readily lose hydrogen chloride. The *stannichloride* also forms yellow needles. The yellow ether (I) does not combine with acids. J. C. C.

Action of Carbon Disulphide and Potassium Hydroxide on Ketones. III. HERMANN APITZSCH [with R. BLEZINGER] (*Ber.*, 1908, 41, 4028-4039. Compare *Abstr.*, 1904, i, 510; 1905, i, 810).—Ethyl acetonediacarboxylate reacts with carbon disulphide and potassium hydroxide, yielding the dipotassium salt of *ethyl 2:6-dithiolthiopyrone-3:5-dicarboxylate* [*2:6-dithiol-4-ketopenthiophen-3:5-dicarboxylate*],  $\text{CO} \begin{smallmatrix} \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{SH}) \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{SH}) \end{smallmatrix} \text{S}$ ; the free ester, obtained by treating the potassium salt with dilute sulphuric acid, crystallises from ethyl acetate or from a mixture of chloroform and light petroleum in golden-yellow plates, m. p.  $130^\circ$ , after sintering at about  $118^\circ$ . The *potassium* salt,  $\text{C}_{11}\text{H}_{10}\text{O}_5\text{S}_2\text{K}_2 \cdot \text{EtOH}$ , crystallises from a mixture of alcohol and ether in small, pale yellow, nodular masses, and the *silver* salt forms a yellow, curdy precipitate. The *diethyl ether*,  $\text{C}_5\text{OS}(\text{CO}_2\text{Et})_2(\text{SEt})_2$ ,

crystallises from dilute alcohol in colourless needles, m. p. 47—49°; the *dimethyl ether*,  $C_{13}H_{16}O_5S_3$ , in similar needles, m. p. 82—83°. The *dibenzoyl* derivative,  $C_6OS(CO_2Et)(S \cdot CPh)_2$ , forms prismatic crystals, m. p. 128—129°. The *ammonium* salt,  $C_6OS(CO_2Et)_2(SNH_4)_2$ , forms yellow crystals, is readily soluble in water or alcohol, and readily loses ammonia when exposed to the air. When the ethyl ester of the dithiol is heated with aqueous ammonia for four hours at 100°, the *ammonium* salt,  $CO \begin{smallmatrix} \diagup C(CO_2Et)=C(SNH_4) \\ \diagdown C(CONH_2):C(SNH_4) \end{smallmatrix} > S$ , is obtained as pale yellow tetrahedra, but at 120° the *ammonium* salt,



is obtained as yellow, rhombohedral crystals. The corresponding *acid*,  $C_7H_6O_5N_2S_3$ , crystallises from glacial acetic acid in yellow crystals. When reduced, the dithiol yields *ethyl 4-ketotetrahydropenthiophen-3:5-dicarboxylate*,  $CO \begin{smallmatrix} \diagup CH(CO_2Et) \cdot CH_2 \\ \diagdown CH(CO_2Et) \cdot CH_2 \end{smallmatrix} > S$ ; this crystallises from dilute methyl alcohol in colourless needles, m. p. 102—103°, which are insoluble in alkalis. When oxidised with nitric acid in acetic acid solution, the dithiol yields a termolecular *sulphide*,  $C_{33}H_{32}O_{15}S_9$ , which separates from ethyl acetate in colourless, rhombic crystals, m. p. 185° (compare Fromm and Baumhauer, Abstr., 1908, i, 703).

A *tetrapotassium* salt,  $CO \begin{smallmatrix} \diagup C(CO_2K):C(SK) \\ \diagdown C(CO_2K):C(SK) \end{smallmatrix} > S$ , is formed when the dithiol is hydrolysed with aqueous alcoholic potash under pressure. It forms a greenish-yellow, crystalline mass, and contains  $6H_2O$ . It has not been found possible to isolate the corresponding tetrabasic acid, but the *dimethyl ether*,  $C_5OS(CO_2H)_2(SMe)_2$ , obtained by the action of methyl iodide or methyl sulphate on the potassium salt, crystallises from nitrobenzene in yellow needles, m. p. 230° (decomp.). The corresponding *silver* salt,  $C_5H_6O_5S_3Ag_2$ , crystallises in colourless needles. The *diethyl ether*,  $C_5OS(CO_2H)_2(SEt)_2$ , forms colourless crystals, m. p. 178—180°, and is much more readily soluble than the methyl ester.

When an aqueous solution of the tetrapotassium salt is mixed with acetic and hydrochloric acids, a precipitate of 2:6-dithiol-4-ketopenthiophen-3-carboxylic acid,  $CO \begin{smallmatrix} \diagup CH=C(SH) \\ \diagdown C(CO_2H):C(SH) \end{smallmatrix} > S$ , is obtained; it crystallises from benzene in yellow needles, m. p. 143° (decomp.). The *tripotassium* salt is extremely readily soluble in water or alcohol; the *diethyl ether*,  $C_5HOS(CO_2H)_2(SEt)_2$ , forms colourless needles, m. p. 129—131°, and the *dimethyl ether*,  $C_5H_8O_5S_3$ , has m. p. 215—216°.

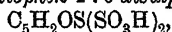
J. J. S.

**Thio- $\gamma$ -pyronedithiols [4-Ketopenthiophendithiols].** HERMANN APITZSCH and G. A. BAUER (*Ber.*, 1908, 41, 4039—4047).—The compound obtained by exposing 3:5-diphenylthiopyrone-2:6-dithiol (4-keto-3:5-diphenylpenthiophen-2:6-dithiol, Abstr., 1905, i, 810) to sunlight is shown to be a termolecular sulphide, formed by the oxidising action of the atmosphere on the dithiol. The same compound is formed when an acetic acid solution of the dithiol is treated with ferric chloride,

halogens, nitric acid, nitrous acid, or hydrogen peroxide. Similar sulphides are formed from ketomethylthiophen-2:6-dithiophen-3:5-dicarboxylic acid (Abstr., 1904, i, 310), but have not been obtained pure. The alkali or alkali-earth salts of the dithiols are oxidised by hydrogen peroxide in neutral or alkaline aqueous solution to disulphonic or disulphinic acids. Fusion with potash transforms the sulphonic acid from ketodiphenylthiophen-2:6-dithiophen-3:5-dicarboxylic acid into phenylacetic acid.

The *sulphide* from ketodiphenylthiophen-2:6-dithiophen-3:5-dicarboxylic acid,  $C_{51}H_{32}O_8S_9$ , is deposited from a mixture of benzene and light petroleum in crystals, m. p.  $284^\circ$ , but when crystallised from chloroform or acetic acid has m. p.  $278^\circ$ . It is converted by alkalis, sodium thiosulphate, or hydriodic acid to the original dithiol.

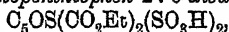
4-Keto-3:5-diphenylthiophen-2:6-disulphonic acid,



crystallises from its concentrated aqueous solution in colourless, hygroscopic needles, m. p.  $261^\circ$ . The *sodium* salt crystallises from a mixture of alcohol and ether with 2EtOH. The *barium* salt crystallises in needles with 2EtOH, or with  $12H_2O$  in large, glistening prisms. The *silver* salt,  $C_{11}H_{10}O_7S_3Ag_2$ , crystallises from hot water in glistening rods. The *dimethyl* ester,  $C_{19}H_{16}O_8S_3$ , crystallises from warm acetone in colourless plates, m. p.  $190-191^\circ$ , and the *ethyl* ester has m. p.  $173-174^\circ$ .

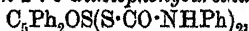
*Sodium* 4-keto-3-methylthiophen-2:6-disulphonate crystallises with 1EtOH, and the corresponding salt of the 3:5-dimethyl acid with  $3H_2O$ .

3:5-Dicarbethoxy-4-ketopenthiophen-2:6-disulphonic acid,



obtained from ethyl 4-keto-2:6-dithiophen-3:5-dicarboxylate (see preceding abstract), forms a *sodium* salt,  $C_{11}H_{10}O_{11}S_3Na_2 \cdot H_2O$ , which crystallises in colourless needles. When the barium salt of the dithiol is oxidised, *barium* 3:5-dicarbethoxy-4-ketopenthiophen-2:6-disulphonate,  $C_{11}H_{10}O_9S_3Ba$ , is obtained, unless an excess of barium carbonate and hydrogen peroxide is present, when the corresponding *sulphonate*,  $C_{11}H_{10}O_{11}S_3Ba \cdot 2H_2O$ , is formed.

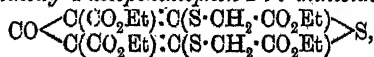
When boiled with aniline, the diphenyl dithiol is decomposed, and yields diphenylcarbamide and malonanilide; when mixed with a benzene solution of phenylcarbimide, it yields the urethane, 4-keto-3:5-diphenylthiophen-2:6-dithiophenylurethane,



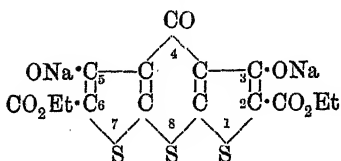
m. p.  $135^\circ$  (decomp.).

3:5-Dicarbethoxy-4-ketopenthiophen-2:6-dithiophenylurethane has m. p.  $140^\circ$ . J. J. S.

Condensation of Esters of 4-Keto-2:6-dithiophen-3:5-dicarboxylic Acid with Ethyl Chloroacetates. HERMANN APITZSCH (Ber., 1908, 41, 4047-4052).—Ethyl chloroacetate readily reacts with a hot alcoholic solution of the sodium salt of ethyl 2:6-dithiophen-3:5-dicarboxylate (this vol., i, 46), yielding ethyl 3:5-dicarbethoxy-4-ketopenthiophen-2:6-dithiolacetate,



as a viscid, heavy oil, which reacts with aqueous or alcoholic sodium hydroxide, yielding the sodium derivative of *ethyl 3:5-dihydroxy-4-ketopenthiophendithiophen-2:6-dicarboxylate* (annexed constitution) as an amorphous, reddish-yellow powder. The free *dihydroxy*-compound,  $C_{15}H_{12}O_7S_8$ , crystallises from hot alcohol in pale yellow, strongly



refractive, rhombic plates, m. p.  $242^\circ$ , after sintering at  $232^\circ$ . The corresponding *diethyl ether*,  $C_{19}H_{20}O_7S_8$ , forms colourless needles, m. p.  $217-218^\circ$ ; the *dibenzoate*,  $C_{29}H_{20}O_9S_8$ , sinters at  $263^\circ$  and melts at  $267^\circ$ .

When methyl chloroacetate is condensed with the dithiol, a certain amount of *methyl 3:5-dicarbethoxy-4-ketopenthiophen-2:6-dithiolacetate*,  $C_{14}H_{10}O_7N_2$ , is obtained. It forms slender, pale yellow needles, m. p.  $245^\circ$ , after sintering at  $220^\circ$ , and yields a *dibenzoate*,  $C_{28}H_{18}O_9S_8$ , m. p.  $270.5^\circ$ , after sintering at  $267^\circ$ . *Methyl 3:5-dihydroxy-4-ketopenthiophendithiophen-2:6-dicarboxylate*,  $C_{13}H_8O_7S_8$ , crystallises from ethylene dibromide or from much chloroform in straw-yellow needles, m. p.  $294^\circ$ . Its *dibenzoate*,  $C_{27}H_{16}O_9S_8$ , has m. p.  $297-298^\circ$ .

The corresponding *diamyl ester*,  $C_9OS_8(OH)_2(CO_2 \cdot C_5H_{11})_2$ , has m. p.  $182^\circ$ , and yields a *dibenzoate*,  $C_{35}H_{32}O_9S_8$ , m. p.  $202-203^\circ$ . J. J. S.

**Double Fluorides of Titanium.** JOHN A. SCHAEFFER (*J. Amer. Chem. Soc.*, 1908, 30, 1862—1865).—The following double fluorides of titanium with alkaloïds have been prepared in the hope of discovering an improved method for separating titanium from columbium and tantalum. *Quinine titanium fluoride*,  $C_{20}H_{24}O_2N_2 \cdot 2H_2TiF_6 \cdot H_2O$ ; the *strychnine salt*,  $2C_{21}H_{22}O_2N_2 \cdot H_2TiF_6 \cdot 3H_2O$ ; the *quinidine salt*,  $2C_{20}H_{24}O_2N_2 \cdot H_2TiF_6 \cdot 4H_2O$ ; the *brucine salt*,

$4C_{23}H_{26}O_4N_2 \cdot 2H_2TiF_6 \cdot 13H_2O$ ; the *cinchonidine salt*,  $C_{19}H_{22}ON_2 \cdot H_2TiF_6 \cdot 2H_2O$ ; the *narcotine salt*,  $2C_{22}H_{25}ON_2 \cdot H_2TiF_6 \cdot 3H_2O$ ; the *cinchonine salt*,  $C_{19}H_{22}ON_2 \cdot H_2TiF_6$ ; the *narceine salt*,  $3C_{23}H_{27}O_3N_2 \cdot H_2TiF_6 \cdot 5H_2O$ ; the *morphine salt*,  $4C_{17}H_{19}O_3N_2 \cdot 2H_2TiF_6 \cdot 5H_2O$ ; the *codeine salt*,

$8C_{18}H_{21}O_3N_2 \cdot 4H_2TiF_6 \cdot 3H_2O$ ; the *papaverine salt*,  $8C_{20}H_{21}O_4N_2 \cdot 4H_2TiF_6 \cdot 3H_2O$ ; and the *apomorphine salt*,  $2C_{17}H_{17}O_3N_2 \cdot H_2TiF_6 \cdot 4H_2O$ .

*Aniline titanium fluoride*,  $2C_6H_5 \cdot NH_2 \cdot H_2TiF_6 \cdot H_2O$ , forms pink needles. E. G.

**Isomerism of Ephedrine and  $\psi$ -Ephedrine.** JOHANNES GADAMER (*Arch. Pharm.*, 1908, 246, 566—574).—Emde's representa-

tion of ephedrine and  $\psi$ -ephedrine by the formulæ:  $Me \cdot \overset{OH}{\underset{H}{C}} - \overset{HNMe}{\underset{H}{C}} \cdot Ph$

and  $Me \cdot \overset{OH}{\underset{H}{C}} - \overset{H}{\underset{HNMe}{C}} \cdot Ph$  respectively is accepted, but his explanation of

the reversible conversion of the one isomeride into the other by the

action of hot hydrochloric acid, as due to racemisation in the right-hand half of the molecule as represented by the above formulæ, is inadmissible (Abstr., 1908, i, 203). The chief grounds for this opinion are: (1) that taking account of the relative weights of the atoms and atomic complexes concerned, and assuming racemisation to occur in the right-hand portion of the molecule only, ephedrine would be dextrorotatory instead of levorotatory, as it actually is; (2) Emde's explanation would imply that by adding a further complex to the right-hand portion of the molecule, the dextrorotation of  $\psi$ -ephedrine should be increased, but  $\psi$ -ephedrylphenylthiocarbamide, although still dextrorotatory, has a lower rotation than either  $\psi$ -ephedrine or its hydrochloride. These difficulties disappear if racemisation is assumed to occur in the left-hand portion of the molecule, as represented above.

*Ephedrylphenylthiocarbamide*, m. p.  $115^{\circ}$  (decomp.),  $[\alpha]_D^{20} - 105.1^{\circ}$  in alcohol, crystallises from alcohol in rosettes of prisms.  *$\psi$ -Ephedrylphenylthiocarbamide*, m. p.  $122^{\circ}$ ,  $[\alpha]_D^{20} + 22.8^{\circ}$  in alcohol, crystallises from alcohol in transparent, rectangular tablets. T. A. H.

**apoMorphine Hydrochloride.** ERNST SCHMIDT and R. GAZE (*Chem. Zentr.*, 1908, ii, 1187; from *Apoth. Zeit.*, 1908, 23, 657—658).—The authors find that this substance when dried in a desiccator or at  $100^{\circ}$  contains 3.61—3.95% of water, and is not anhydrous, as stated by Matthiesen and Wright (*Annalen, Sup.* 7, 172). The amount of water found present is in close agreement with both of the following formulæ:  $2(C_{17}H_{17}O_2N, HCl), H_2O$  or  $C_{17}H_{17}O_2N, HCl, H_2O$ .

Anhydrous *apomorphine* hydrochloride darkens in colour when heated above  $200^{\circ}$ , and does not melt below  $250^{\circ}$ . As characteristic of this substance, it is stated that one drop of ferric chloride solution (1:10) gives a blue coloration to 10 c.c. of an aqueous solution of the hydrochloride (1:10,000). Further, that 10 c.c. of this *apomorphine* hydrochloride solution with 1 c.c. chloroform, rendered alkaline by sodium hydroxide, and shaken with air, gives a reddish-violet colour to the aqueous portion, and a blue colour to the chloroform portion, of the mixture. J. V. E.

**Morpholones.** ERNEST FOURNEAU (*Bull. Soc. chim.*, 1908, [iv], 3, 1141—1145).—The publication by Wolfenstein with Mamlock (Abstr., 1908, i, 281), and with Rolle (*ibid.*, 282) of the results obtained in condensing haloid acid chlorides with tropine has led the author to give an account of the different results he has obtained in condensing  $\alpha$ -halogenated acid chlorides with  $\alpha\beta$ -amino-alcohols.

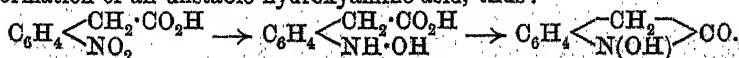
Dimethylaminodimethylethylcarbinol (Süsskind, Abstr., 1906, i, 133) condenses, when warmed during two hours at  $100^{\circ}$ , with ethyl phenylbromoacetate to form *phenylmethylethylmorpholonedimethylammonium bromide*,  $\begin{array}{c} CH_2 \cdot NMe_2 \cdot Br \cdot CHPh \\ | \\ CMeEt - O - CO \end{array}$ , m. p.  $195^{\circ}$ , which crystallises from alcohol, is soluble in water, but nearly insoluble in acetone, and has a very bitter taste. With moist silver hydroxide, it furnishes the corresponding substituted *ammonium hydroxide*, m. p.  $163^{\circ}$ , which

is crystalline and very bitter, readily soluble in water or chloroform, and is neutral to litmus. On heating, both the bromide and the hydroxide, the former with the loss of methyl bromide, and the latter with the loss of methyl alcohol, form the corresponding *tertiary* base,  $\text{CH}_2\cdot\text{NMe}\cdot\text{CHPh}$   
 $\text{CMeEt}\cdot\text{O}\cdot\text{CO}$ , m. p. about  $650^\circ$  (?), b. p.  $187^\circ/12$  mm. or  $210^\circ/33$  mm., which crystallises from light petroleum and furnishes a *picrate*, m. p.  $138^\circ$ , and an *aurichloride*, m. p. about  $98^\circ$ . With boiling baryta water, the base yields the corresponding *hydroxyamino-acid*,  $\text{OH}\cdot\text{CEtMe}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ . T. A. H.

**Surinamine.** H. BLAU (*Zeitsch. physiol. Chem.*, 1908, 58, 153—155. Compare Hiller-Bombien, Abstr., 1893, i, 182).—The base forms colourless, glistening needles, begins to decompose at  $233^\circ$ , and is completely molten at  $246^\circ$ . When subjected to dry distillation, it yields a sublimate, from which a *platinichloride*, (Pt, 27.5%), m. p.  $205^\circ$ , was obtained. When fused with potash, the base yields *p*-hydroxybenzoic acid. J. J. S.

**Synthesis of Tertiary Pyridylalkines [Pyridyldialkylcarbinols] and their Derivatives.** WLADISLAW SOBECKI (*Ber.*, 1908, 41, 4103—4110).—The interaction of magnesium methyl iodide ( $3\frac{1}{2}$  mols.) and ethyl picolinate in dry ether leads to the formation of *dimethyl- $\alpha$ -pyridylalkine* [*2-pyridyldimethylcarbinol*],  $\text{C}_5\text{NH}_4\cdot\text{CMe}_2\cdot\text{OH}$ , m. p.  $50$ — $51^\circ$ , b. p.  $204$ — $205^\circ$  (corr.) or  $83.5$ — $84^\circ/10$  mm.; the *platinichloride*, *aurichloride*, and *picrate* have m. p.  $178^\circ$ ,  $117$ — $118^\circ$ , and  $100$ — $101^\circ$  respectively. Similarly, magnesium ethyl bromide and ethyl nicotinate yield *3-pyridyldiethylcarbinol*,  $\text{C}_5\text{NH}_4\cdot\text{CEt}_2\cdot\text{OH}$ , b. p.  $152$ — $155^\circ/24$  mm., which forms a *platinichloride*, which decomposes at  $199^\circ$ , an *aurichloride*, m. p.  $108^\circ$ , and a *picrate*, m. p.  $112$ — $113^\circ$ . The reduction of 2-pyridyldimethylcarbinol by sodium and alcohol yields *isopropylpiperidine* and 2-piperidyldimethylcarbinol,  $\text{C}_5\text{NH}_{10}\cdot\text{CMe}_2\cdot\text{OH}$ , b. p.  $209$ — $210^\circ$  (corr.) or  $92.5$ — $93^\circ/12$  mm.,  $D_4^{15}$  0.9787, which forms a *picrate*, m. p.  $139^\circ$ , *aurichloride*, m. p.  $128$ — $129^\circ$ , and a *platinichloride*, which decomposes at  $185^\circ$ . When heated with phosphoric oxide, 2-piperidyldimethylcarbinol loses water in two ways, yielding *isopropyl- $\Delta^2$ -piperidine*, identical with Ladenburg's compound (Abstr., 1887, 740), and  *$\alpha$ -methovinylopiperidine*,  $\text{C}_5\text{NH}_{10}\cdot\text{CMe}\cdot\text{CH}_2$ , which are separated by means of their *picrates*. Methovinylopiperidine forms a *hydrochloride*,  $\text{C}_5\text{H}_{15}\text{N}\cdot\text{HCl}$ , m. p.  $193^\circ$ , a *platinichloride*, decomposing at  $175$ — $176^\circ$ , and is resolved by *d*-tartaric acid, the regenerated bases, slightly diluted with ether, showing a  $1.4^\circ$  in a 3 cm. tube and  $-0.9^\circ$  in a 5 cm. tube respectively. C. S.

**N-Hydroxyindole Derivatives from o-Nitrophenylacetic Acid.** ARNOLD REISSERT (*Ber.*, 1908, 41, 3921—3931).—When *o*-nitrophenylacetic acid is reduced with zinc dust and dilute sulphuric acid at  $28$ — $34^\circ$ , 1:2-dioxindole is obtained with the probable intermediate formation of an unstable hydroxyamino-acid, thus:

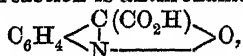


When the reduction is effected in neutral solution with the addition of ammonium chloride, there is also formed *o*-azoxyphenylacetic acid,  $\text{ON}_2(\text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$ , in yellow needles, m. p. 250—251° (decomp.). The reduction in acid solution may be carried out with a solution of *o*-nitrophenylacetic acid, prepared by oxidising *o*-nitrophenylpyruvic acid with hydrogen peroxide; a small amount of oxindole (m. p. 126°, not 120° as given in the literature) is also formed.

1:2-Dioxindole crystallises from water in small, hard, colourless rhombs; when a drop of ferric chloride is added to its cold aqueous solution, a characteristic blue coloration is produced.

1-Methoxyoxindole,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{N(OMe)} \end{smallmatrix} \text{CO}$ , prepared by treating dioxindole with methyl sulphate, forms slender, colourless rods or feathery crystals, m. p. 88.5°. 1-Acetoxoxindole crystallises in colourless needles, m. p. 101°.

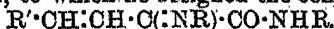
1-Benzoyloxyoxindole forms small, pale red crystals, m. p. 124—125°. 1-Hydroxyisatoxime,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C(N·OH)} \\ \text{N(OH)} \end{smallmatrix} \text{CO}$ , prepared by boiling dioxindole with aqueous sodium nitrite, forms small, yellow needles, m. p. 223° (decomp.) with previous sintering; the sodium salt is described. 1-Methoxyisatoxime, prepared by treating methoxyoxindole with nitrous acid and subsequently adding sodium hydroxide, crystallises in small, yellow needles, m. p. 172°. 1-Hydroxyisatin,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \text{N(OH)} \end{smallmatrix} \text{CO}$ , is formed in small amount (recognised by the preparation of the phenylhydrazone) when hydroxyisatoxime is reduced with zinc and ammonia and subsequently oxidised with ferric chloride; the chief product of the reaction is anthroxanic acid,



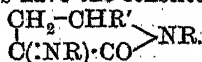
m. p. 196° (decomp.), which is also formed by boiling the oxime with dilute hydrochloric acid.

J. C. C.

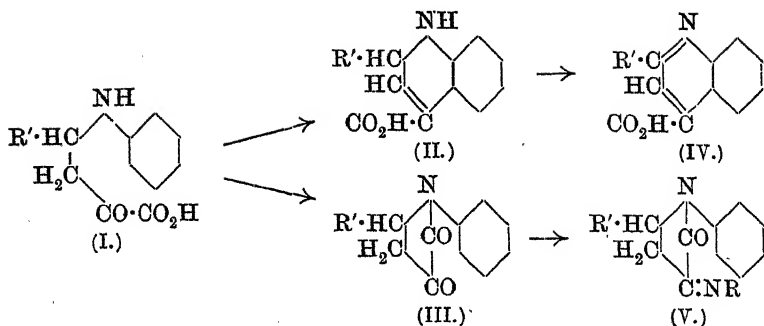
Synthesis of  $\alpha$ -Substituted Cinchonic Acids by Doebner's Method. WALTHER BORSCHKE (*Ber.*, 1908, 41, 3884—3894).—By the interaction of a primary, aromatic amine containing a free ortho-position, pyruvic acid, and an aldehyde, Doebner (*Abstr.*, 1888, 299) found that, in addition to an  $\alpha$ -substituted dihydrocinchonic acid, compounds were formed, to which he assigned the constitution



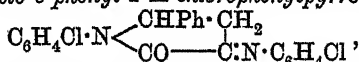
From experiments on phenylpyruvic acid, however, the author finds that these compounds have the constitution



The first stage of the interaction consists in the formation of a  $\gamma$ -anilino- $\alpha$ -ketonic acid (I), which loses water in two ways, giving the compounds (II) and (III). The former then loses hydrogen, yielding the cinchonic acid (IV), and the latter condenses with a second mol. of the base to form the anil (V).

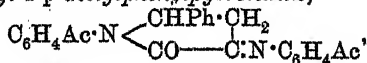


*2-Phenyl-7-methylcinchonic acid*,  $C_9NH_4MePh \cdot CO_2H$ , prepared by condensing benzaldehyde, *m*-toluidine, and pyruvic acid in alcoholic solution, forms a white, crystalline powder, m. p. 212—214°. *7-Hydroxy-2-phenylcinchonic acid*,  $C_9NH_4Ph(OH) \cdot CO_2H$ , similarly prepared from *m*-aminophenol, crystallises from hot dilute hydrochloric acid as a yellow, crystalline powder, m. p. 333—334°; carbon dioxide is lost at the m. p., with the formation of *7-hydroxy-2-phenylquinoline*, which crystallises in pale yellow needles, m. p. 229—230°. *7-Chloro-2-phenylcinchonic acid*,  $C_9NH_4ClPh \cdot CO_2H$ , prepared from *m*-chloroaniline, best in glacial acetic acid solution, forms colourless needles, m. p. 244—246° (decomp.); in the same reaction there is also formed *3-m-chloroanilo-2-keto-5-phenyl-1-m-chlorophenylpyrrolidine*,



crystallising in small, colourless needles, m. p. 199—200°. Similarly, by the use of *p*-chloroaniline, there is obtained a mixture of *6-chloro-2-phenylcinchonic acid*, white, crystalline grains, darkening at 225°, m. p. 243°, and *3-p-chloroanilo-2-keto-5-phenyl-1-p-chlorophenylpyrrolidine*, colourless needles, m. p. 203—204°.

When *p*-aminoacetophenone is condensed with benzaldehyde and pyruvic acid in alcoholic solution, there is formed *3-p-acetylanilo-2:3-diketo-5-phenyl-1-p-acetylphenylpyrrolidine*,



small, colourless needles, m. p. 238—239°. By carrying out the reaction in glacial acetic acid solution, *7-acetyl-2-phenylcinchonic acid* is formed in small, colourless needles, m. p. 200°.

*o*-Nitroaniline does not condense with pyruvic acid and either benzaldehyde or *m*-nitrobenzaldehyde.

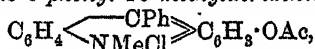
The interaction of benzaldehyde, pyruvic acid, and *m*-nitroaniline leads to the formation of *3-m-nitroanilo-2-keto-5-phenyl-1-m-nitrophenylpyrrolidine*,  $NO_2 \cdot C_6H_4 \cdot N \begin{cases} CHPh \cdot CH_2 \\ CO - C:N \cdot C_6H_4 \cdot NO_2 \end{cases}$ , yellow needles, m. p. 212° (decomp.), and when *p*-nitroaniline is used in alcoholic solution, *2:3-diketo-5-phenyl-1-p-nitrophenylpyrrolidine*, yellow needles, m. p. 188—189°, is obtained. The *3-p-nitroanilo*-derivative is formed

in glacial acetic or formic acid solution; it crystallises in small, yellow, glistening needles, m. p. 220—221° (decomp.). J. C. C.

**Derivatives of 5-Phenylacridine.** FRIEDRICH KEHRMANN and A. STÉPANOFF (*Ber.*, 1908, 41, 4133—4141).—The object of the present investigation is to obtain in the acridine series the analogues of the rosindones, prasindones, etc.

Hess and Bernthsen's method for the preparation of 3-amino-5-phenylacridine (Abstr., 1885, 800) has been improved by the use of the benzoyl derivative of *p*-aminodiphenylamine instead of the base itself. The interaction of *p*-benzoylaminodiphenylamine, benzoic acid, and anhydrous zinc chloride for twelve hours at 215—220° leads to the production of 3-amino-5-phenylacridine, m. p. 204°, its benzoyl derivative (compare Ullmann and Ernst, Abstr., 1906, i, 205), 3-hydroxy-5-phenylacridine (Hess and Bernthsen, *loc. cit.*), and a substance,  $C_{28}H_{26}N_4$ , m. p. 308°, which is possibly diaminodiphenyl-diacyridine.

3-Acetylamino-5-phenylacridine, dissolved in nitrobenzene, is treated with methyl sulphate at 150°, and the precipitate, obtained by the addition of ether to the cooled solution, is dissolved in luke-warm water; by the addition of concentrated hydrochloric acid or sodium chloride, 3-acetylamino-5-phenyl-10-methylacridinium chloride,



is obtained, which forms orange-yellow crystals, and gives a yellow, fluorescent aqueous solution. The *platinichloride*,  $(C_{22}H_{19}ON_2)_2PtCl_6$ , forms golden-yellow, slender crystals. When a solution of the chloride is partly evaporated with hydrochloric acid, neutralised with ammonium carbonate, and treated with solid sodium nitrate, 3-amino-5-phenyl-10-methylacridinium nitrate,  $C_{20}H_{17}N_2 \cdot NO_3$ , is obtained, which crystallises in reddish-black needles, and forms a blood-red, non-fluorescent solution in water and alcohol; the *platinichloride*,  $(C_{20}H_{17}N_2)_2PtCl_6$ , is a dark red, crystalline powder. 3-Acetyloxy-5-phenyl-10-methylacridinium *platinichloride*,  $(C_{22}H_{19}O_2N_2)_2PtCl_6$ , is a citron-yellow, crystalline powder, obtained in a similar manner to the acetylamino-salt. 3-Hydroxy-5-phenyl-10-methylacridinium chloride crystallises in long, golden-yellow needles, and, in not too dilute aqueous solution, yields with sodium carbonate or ammonium

hydroxide the base,  $C_6H_4 \begin{array}{c} \text{CPh} \\ \text{NMe(OH)} \end{array} C_6H_5 \cdot OH$ , which crystallises in reddish-black needles, and loses  $1H_2O$  at 120°. It is doubtful whether the resulting anhydride is analogous to the prasindones, since the prasindone hydrates of the azonium series do not anhydriise by heating (Abstr., 1908, i, 297). C. S.

**Dianthraquinonylphenylenediamine.** IV. EDUARD LAUBÉ and C. KÖNIG (*Ber.*, 1908, 41, 3874—3879).—Further derivatives of *p*-phenylenebis-1-aminoanthraquinone have been prepared, and the investigation extended to the corresponding *o*-phenylene compounds (compare Laubé, Abstr., 1907, i, 941).

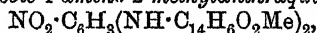
1-*p*-Nitroanilino-2-hydroxyanthraquinone,  $C_{20}H_{12}O_5N_2$ , prepared by boiling together 1-chloro-2-hydroxyanthraquinone, *p*-nitroaniline, potass-

ium carbonate, and copper acetate in nitrobenzene, is a dark brown powder, m. p.  $342^{\circ}$  (corr.). It is reduced by an aqueous solution of sodium sulphide to 1-*p*-aminoanilino-2-hydroxyanthraquinone,  $C_{20}H_{14}O_2N_2$ , a black powder with a high m. p. The latter compound condenses with 1-chloro-2-hydroxyanthraquinone when the two substances are boiled with copper powder in nitrobenzene, forming *p*-phenylenebis-1-amino-2-hydroxyanthraquinone,  $C_6H_4(NH \cdot C_{14}H_9O_2 \cdot OH)_2$ , a brownish-black powder, m. p. above  $360^{\circ}$ .

The following compounds are obtained by similar methods: 1-*p*-Bromoanilino-2-methylanthraquinone,  $C_{21}H_{15}O_2NBr$ , crystallises in small, scarlet needles, m. p.  $190^{\circ}$  (corr.). *p*-Phenylenebis-1-amino-2-methylanthraquinone,  $C_{36}H_{24}O_4N_2$ , is a black powder, giving a violet mark on porcelain, and has a high m. p.

1-*o*-Chloro-*p*-nitroanilino-2-methylanthraquinone,  $C_{21}H_{13}O_4N_2Cl$ , crystallises in glistening, coppery leaflets, m. p.  $272-273^{\circ}$  (corr.).

*p*-Nitro-*o*-phenylenebis-1-amino-2-methylanthraquinone,



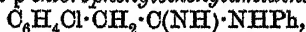
is a brownish-black powder with a high m. p.

1-*o*-Acetylaminonaphthylaminanthraquinone,  $C_{26}H_{18}O_3N_2$ , prepared from 1-aminoanthraquinone and 2-chloro-1-acetylaminonaphthalene, is a brown powder with a high m. p. It yields, on hydrolysis, 1-*o*-aminonaphthylaminanthraquinone (1-anthraquinonyl-*o*-naphthylendiamine), a black powder which condenses with 1-chloroanthraquinone, forming *o*-naphthylenebis-1-aminoanthraquinone,  $C_{10}H_6(NH \cdot C_{14}H_9O_2)_2$ , a brownish-black powder, m. p.  $350^{\circ}$ . W. H. G.

**Amidines.** LXXXVIII. REINHOLD VON WALTHER and A. GROSSMANN (*J. pr. Chem.*, 1908, [ii], 78, 478—496).—A further contribution to the chemistry of the amidines.

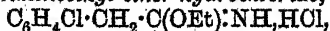
Phenylacetonitrile readily interacts with aniline, but not with the chloroanilines, although the latter readily form amidines with benzonitrile. Similarly, *p*-chlorophenylacetonitrile does not combine readily with aniline.

*p*-Chlorophenylacetonitrile, when heated with aniline hydrochloride at  $180^{\circ}$ , yields phenyl-*p*-chlorophenylethenylamidine,



which crystallises in glistening leaflets, m. p.  $153-154^{\circ}$ ; it may also be prepared (1) by the action of aniline on the imino-chloride obtained by treating *p*-chlorophenylacetamide with phosphorus pentachloride; (2) by treating a solution of *p*-chlorophenylacetonitrile (2 mols.) and aniline (1 mol.) in benzene with sodium (2 mols.); the hydrochloride has m. p.  $213-214^{\circ}$ ; the sulphate forms small needles, m. p.  $185^{\circ}$ ; the platinumchloride,  $C_{38}H_{26}N_4Cl_2 \cdot H_2PtCl_6$ , crystallises in small, orange prisms, m. p.  $185^{\circ}$  (decomp.).

*p*-Chlorophenylacetiminioethyl ether hydrochloride,



obtained by the action of hydrogen chloride on an alcoholic solution of *p*-chlorophenylacetonitrile, crystallises in small, slender needles, m. p.  $170-173^{\circ}$ ; it is converted by aniline at  $35^{\circ}$  into diphenyl-*p*-chlorophenylethenylamidine,  $C_6H_4Cl \cdot CH_2 \cdot C(NPh) \cdot NHPh$ , small, slender needles, m. p.  $97-98^{\circ}$ .

Phenylacetonitrile and *p*-chloroaniline, when heated together, yield *o*-phenyl-*p*-chloroacetanilide,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , glistening needles, m. p. 163—164°, and phenyl-*p*-chlorophenylethenylamidine,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , white needles, m. p. 112—113°; the hydrochloride of the latter crystallises in prisms, m. p. 106—108°. The following amidines were prepared by similar methods.

Phenyl-*m*-chlorophenylethenylamidine,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , crystallises in needles, m. p. 91—93°; the hydrochloride forms glistening needles, decomposing at 205—220°; the sulphate forms rectangular plates, m. p. 179—181°; the nitrate forms needles, m. p. 108—109°.

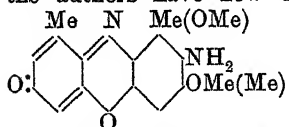
*m*-Chlorophenylbenzenylamidine,  $\text{NH}\cdot\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , crystallises in prisms and needles, m. p. 115—116°; the hydrochloride crystallises with  $\text{H}_2\text{O}$ , and has m. p. 95°; the anhydrous salt has m. p. 186—189°; the picrate has m. p. 134—135°; the platinichloride has m. p. about 195° (decomp.). The hydrochloride is converted by water under pressure at 170° into benzoyl *m*-chloroaniline. The dibenzoyl derivative,  $\text{NBz}\cdot\text{CPh}\cdot\text{NBz}\cdot\text{C}_6\text{H}_4\text{Cl}$ , has m. p. 139°; the phenylcarbamide derivative,  $\text{NHPh}\cdot\text{CO}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , is obtained by acting on the amidine with phenylcarbimide, and crystallises in small prisms, m. p. 172—173°; the phenylthiocarbamide derivative,  $\text{NHPh}\cdot\text{CS}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , obtained in a similar manner, crystallises in rhombohedra, m. p. 131—132°. The amidine is converted by hydroxylamine hydrochloride into *m*-chlorophenylbenzenylamino-oxime,  $\text{CPh}\cdot\text{C}(\text{NOH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , which crystallises in rectangular plates, m. p. 85—87°. Phenylhydrazine converts the amidine hydrochloride into the hydrazidine,  $\text{NHPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , pale yellow needles, m. p. 127—128°, the picrate of which has m. p. 155—156° (decomp.). The amidine reacts with picryl chloride, yielding *m*-chlorophenyltrinitrophenylbenzenylamidine,  $\text{NH}\cdot\text{CPh}\cdot\text{N}(\text{C}_6\text{H}_4\text{Cl})\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ , which crystallises in yellow octahedra, m. p. 148° (decomp.).

The following compounds were prepared by the same methods as the corresponding meta-derivatives.

*o*-Chlorophenylbenzenylamidine,  $\text{C}_{13}\text{H}_{11}\text{N}_2\text{Cl}$ , crystallises in needles, m. p. 114—115°; the hydrochloride forms white crystals, m. p. 205—206°; the platinichloride crystallises in dark yellow needles, m. p. 200—202° (decomp.); the picrate has m. p. 193—194°; the dibenzoyl derivative,  $\text{C}_{27}\text{H}_{19}\text{O}_2\text{N}_2\text{Cl}$ , forms needles, m. p. 146—147°; the phenylcarbamide derivative,  $\text{C}_{20}\text{H}_{16}\text{ON}_2\text{Cl}$ , crystallises in glistening leaflets, m. p. 177—178°; the phenylthiocarbamide derivative,  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{SCl}$ , forms yellow needles, m. p. 123—125°. *o*-Chlorophenylbenzenylamino-oxime,  $\text{C}_{13}\text{H}_{11}\text{ON}_2\text{Cl}$ , crystallises with  $\text{Et}\cdot\text{OH}$  in slender needles or prisms, m. p. 163—164°. *o*-Chlorophenylbenzenylphenylhydrazidine,  $\text{C}_{19}\text{H}_{16}\text{N}_3\text{Cl}$ , crystallises in groups of yellow needles, m. p. 93—95°. *o*-Chlorophenyltrinitrophenylbenzenylamidine,  $\text{C}_{19}\text{H}_{12}\text{O}_6\text{N}_5\text{Cl}$ , forms yellow crystals, m. p. 146—148°. W. H. G.

[Action of Amyl Nitrite on Phenyl-*m*-nitrobenzylidenehydrazine.] EUGEN BAMBERGER and WILHELM PEMSEL (*Ber.*, 1908, 41, 4246—4249. Compare Abstr., 1903, i, 285).—Polemical. A reply to Minunni (Abstr., 1904, i, 91). J. J. S.

**Orcinol Monomethyl Ether and an Oxidation Product of Amino-orcinol Monomethyl Ether (2-Amino-5-hydroxy-3-methoxytoluene).** FERDINAND HENRICH and PAUL ROTERS (*Ber.*, 1908, 41, 4210—4214).—Henrich and Schierenberg have shown (*Abstr.*, 1905, i, 93) that 2-amino-3-hydroxy-5-methoxytoluene is oxidised in alkaline solution by air to a phenoxazine derivative, and the authors have now found that 2-amino-5-hydroxy-3-methoxy-



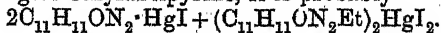
toluene, when oxidised under the same conditions, yields a phenoxazine derivative having the annexed formula.

Orcinol monomethyl ether, previously obtained as an oil (Henrich and Nachti-gall, *Abstr.*, 1903, i, 414), has now been prepared in the crystalline form, m. p. 63°, from the fraction b. p. 256—260°; on adding bromine to its solution in carbon disulphide, a *dibromo*-derivative is formed in white needles, m. p. 113°. 4-Amino-3(5)-methoxy-5(3):7-dimethylphenoxazone,  $C_{15}H_{14}O_3N_2$ , crystallises in red, slender, felted needles or right-angled or six-cornered tablets, m. p. 258—260°; the *dihydrochloride* forms golden leaflets, changing in the air to steel-blue crystals, and the *monoacetyl* derivative is a deep red powder, m. p. 256°.

J. C. C.

**Compounds of Pyrazolones with Mercury Oxide.** J. EURY (*Chem. Zentr.*, 1908, ii, 1037—1038; from *Bul. Sci. Pharmacol.*, 1908, 15, 384—394).—When a boiling alkaline solution of antipyrine is treated with a mercury salt, or with freshly-precipitated mercuric oxide, *mercury antipyrine*,  $(C_{11}H_{11}ON_2)_2Hg \cdot H_2O$ , crystallises from the liquid on cooling. This substance forms colourless, prismatic crystals, m. p. 180° (corr.), having neither taste nor smell, is optically active, and soluble in water at 15° to 0.42%, at 100° to 4.37%, in 10% salt solution at 15° to 1.26%, in cold 90% alcohol to 2.02%, and in boiling 90% alcohol to 43.48%. The aqueous solution of mercury antipyrine reacts weakly alkaline, and shows the characteristic reaction of antipyrine, but, with the exception of hydrogen sulphide, no usual test indicates the presence of mercury.

It is completely soluble in most acids, although hydrochloric and nitric acids produce a white precipitate which is soluble in excess of the acid. With the object of obtaining evidence as to the position of mercury in the molecule, it was treated with ethyl iodide in presence of chloroform, when there was produced a compound of the formula  $C_{48}H_{54}O_4NI_4Hg_3$ , which formed yellow crystals, m. p. 202°. Inasmuch as this substance when treated with hydrogen sulphide or potassium cyanide did not give ethylantipyrine, it is probably



Methyl and propyl iodides behave in a similar manner, giving respectively a pale yellow, crystalline compound, m. p. 186°, and yellow, needle-shaped crystals, m. p. 186°.

Methylphenylpyrazolone, dimethylaminoantipyrine, and diantipyrinemethane reduce freshly-precipitated mercuric oxide in boiling water, whereas: tolylpyrine with mercuric oxide yields mercury

*p*-tolyl dimethylpyrazole [*p*-tolyl dimethylpyrazolone],  
 $(C_{13}H_{13}ON_2)_2Hg, 2H_2O$ ,  
 white crystals, m. p. 187°.

From this it appears that a free hydrogen atom in position 4 conditions the interaction of pyrazolones with mercuric oxide.

J. V. E.

**1-Phenyl-4-alkyl-3:5-pyrazolidones and Antipyrines of the Malonic Acid Series.** AUGUST MICHAELIS and KONRAD SCHENK (*Ber.*, 1908, 41, 3865—3873).—Several derivatives of 1-phenyl-3:5-pyrazolidone (3-hydroxy-1-phenyl-5-pyrazolone) containing an alkyl group in position 4 have been prepared by the method described previously (*Abstr.*, 1907, i, 966). 1-Phenyl-4:4-dimethyl-3:5-pyrazolidone is converted by phosphoryl chloride under pressure at 150° into 3-chloro-1-phenyl-4:4-dimethyl-5-pyrazolone; that is, it reacts in a similar manner to 3-pyrazolone derivatives (compare Michaelis, *Abstr.*, 1905, i, 377), and, like these, yields with methyl iodide an antipyrine-like compound, namely, 1-phenyl-2:4:4-trimethyl-

3:5-pyrazolidone (dimethylmalonylantipyrine), 
$$\begin{array}{c} \text{NMe} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{C} - \text{CMe}_2 \end{array}$$
 or

$$\begin{array}{c} \text{NMe} \cdot \text{NPh} \\ | \quad \diagup \\ \text{CO} - \text{CMe}_2 \end{array} \text{CO.}$$
 This substance was previously described by Michaelis

and Röhmer (*Abstr.*, 1899, i, 233) as 3-methoxy-1-phenyl-4:4-dimethyl-5-pyrazolone, but, since it may also be prepared by the condensation of acetylphenylmethylhydrazine with dimethylmalonic acid in the presence of phosphorus trichloride, it follows that one of the methyl groups must be attached to nitrogen and not to oxygen; consequently, the chief argument in support of the view that 3:5-pyrazolidones are 3-hydroxypyrazolones becomes invalid, although 3:5-pyrazolidones undoubtedly behave in most cases as hydroxy-compounds.

1-Phenyl-2:4:4-trimethyl-3:5-pyrazolidone, unlike other antipyrines, is readily decomposed by aqueous sodium hydroxide, yielding a substance, m. p. 178°, which, originally described by Michaelis and Röhmer (*loc. cit.*), is now shown to be a *s*-phenylmethylhydrazide of dimethylmalonic acid. It also follows from this investigation that the substance, m. p. 70°, obtained by Michaelis and Röhmer by the action of phosphorus pentachloride on the pyrazolidone

is a 5-chloro-3-antipyrine, 
$$\begin{array}{c} \text{NMe} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CCl} \\ \diagdown \quad \diagup \\ \text{C} - \text{CMe} \end{array}$$
 and the acid, m. p. 173°,

derived from the latter is the *s*-phenylmethylhydrazide of methylmalonic acid,  $\text{NHMe} \cdot \text{NPh} \cdot \text{CO} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ .

**3-Benzoyl-1-phenyl-4:4-dimethyl-3:5-pyrazolidone**,  $C_{18}H_{16}O_3N_2$ , prepared by acting on the pyrazolidone in alkaline solution with benzoyl chloride, forms white crystals, m. p. 80°; the corresponding 3-benzene-sulphonyl derivative,  $C_{17}H_{16}O_4N_2S$ , prepared in a similar manner, crystallises in long needles, m. p. 99°.

*Dimethylmalonic acid s-phenylmethylhydrazide*,

$\text{NHMe} \cdot \text{NPh} \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ ,

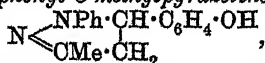
has m. p. 178°; the sodium salt, (2H<sub>2</sub>O), white leaflets, and lead salt, white precipitate, were prepared and analysed.

1-Phenyl-4-ethyl-3:5-pyrazolidone,  $\begin{matrix} \text{CHEt} \cdot \text{CO} \\ \text{CO} - \text{NH} \end{matrix} > \text{NPh}$ , prepared by condensing ethyl malonate with acetylphenylhydrazine in the presence of phosphorus trichloride, forms white needles, m. p. 105°; the dibenzoyl derivative, C<sub>25</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>, crystallises in white prisms, m. p. 120°; the dibenzenesulphonyl derivative, C<sub>23</sub>H<sub>20</sub>O<sub>6</sub>N<sub>2</sub>S<sub>2</sub>, has m. p. 189°. 1-Phenyl-4-ethyl-3:5-pyrazolidone is converted by phosphoryl chloride into 3-chloro-1-phenyl-4-ethyl-5-pyrazolone,  $\begin{matrix} \text{CHEt} \cdot \text{CO} \\ \text{CCl} = \text{N} \end{matrix} > \text{NPh}$ , large, colourless crystals, m. p. 130°, and 3:5-dichloro-1-phenyl-4-ethyl-pyrazole,  $\begin{matrix} \text{CEt} \cdot \text{CCl} \\ \text{CCl} = \text{N} \end{matrix} > \text{NPh}$ , large, white crystals, m. p. 81°. 4-Benzene-azo-1-phenyl-4-ethyl-3:5-pyrazolidone, C<sub>17</sub>H<sub>16</sub>O<sub>2</sub>N<sub>4</sub>, prepared by adding a solution of diazobenzene chloride to the pyrazolidone, crystallises in pale yellow leaflets, m. p. 188°.

1-Phenyl-2:4-dimethyl-4-ethyl-3:5-pyrazolidone (methylethylmalonyl-antipyridine), C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub>, formed by the action of methyl iodide on a solution of the phenylethylpyrazolidone in alcoholic potassium hydroxide, crystallises in colourless leaflets, m. p. 62°, and is converted by aqueous sodium hydroxide into methylethylmalonic acid *s*-phenylmethylethylhydrazide, C<sub>18</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub>, which forms white needles, m. p. 149°, and is reconverted by dehydrating agents into the antipyridine. W. H. G.

**Transformation of Phenylhydrazones of Unsaturated Aldehydes and Ketones into Pyrazolines.** KARL AUWERS and KARL MÜLLER (*Ber.*, 1908, 41, 4230—4233).—The transformation of hydrazones of unsaturated aldehydes and ketones, containing a double linking in the  $\alpha$ -position, is readily effected by means of hot glacial acetic acid.

1-Phenyl-5-*o*-hydroxyphenyl-3-methylpyrazoline,

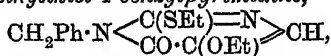


prepared by warming *o*-hydroxybenzylideneacetonephenylhydrazone (m. p. 154°: Harries, *Abstr.*, 1892, 169, gives 159—160°) with glacial acetic acid for half an hour, crystallises in small, compact cubes, m. p. 147—148°. The *O*-benzoate of the above hydrazone forms glistening, yellow needles, m. p. 118—119°, and when warmed with glacial acetic acid for some hours yields the benzoate of the corresponding pyrazoline derivative. This forms stellate clusters of yellow needles, m. p. 125°. 1:5-Diphenylpyrazoline (Laubmann, *Abstr.*, 1888, 726) is similarly obtained from cinnamaldehydephenylhydrazone; when the latter is heated with acetic anhydride, no transformation occurs, but the acetate, C<sub>17</sub>H<sub>16</sub>ON<sub>2</sub>, is formed in white, silky needles or compact prisms, m. p. 149—150°. J. C. C.

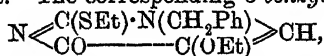
**Pyrimidines. XXXIX. Syntheses of New Derivatives of 5-Hydroxyuracil (isoBarbituric Acid).** TREAT B. JOHNSON and D. BRESEE JONES (*Amer. Chem. J.*, 1908, 40, 538—547).—Johnson

and Clapp (Abstr., 1908, i, 931) have found that 1- and 3-alkyl derivatives of 2:6-dioxytetrahydropyrimidines can be distinguished by their behaviour towards diazobenzenesulphonic acid. This reagent has now been found of use for determining the structure of some 1- and 3-alkyl derivatives of isobarbituric acid.

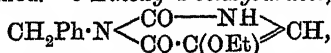
6-Oxy-5-ethoxy-2-ethylthiol-1-benzylpyrimidine,



m. p. 140—141°, obtained by the action of benzyl chloride on 6-oxy-5-ethoxy-2-ethylthiolpyrimidine in presence of potassium hydroxide, forms slender prisms. The corresponding 3-benzyl derivative,



m. p. 85—86°, produced in the same reaction, crystallises in prisms. When the 1-benzyl compound is hydrolysed with concentrated hydrochloric acid, a mixture of 5-ethoxy-1-benzyluracil and 5-hydroxy-1-benzyluracil is obtained. 5-Ethoxy-1-benzyluracil,



m. p. 150°, forms hexagonal prisms, and gives a brilliant red coloration with diazobenzenesulphonic acid in presence of sodium hydroxide. 5-Hydroxy-1-benzyluracil (1-benzylisobarbituric acid), m. p. 230° (decomp.), crystallises in clusters of radiating prisms, and gives the diazobenzenesulphonic acid reaction. When 6-oxy-5-ethoxy-2-ethylthiol-1-benzylpyrimidine is heated with concentrated hydrochloric acid in a sealed tube at 150—160° for three hours, 5-hydroxyuracil (isobarbituric acid),  $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{NH} \\ \text{CO}\cdot\text{C}(\text{OH}) \end{array} \text{CH}$ , is produced. 5-Ethoxy-3-

benzyluracil,  $\text{NH} \begin{array}{c} \text{CO}\cdot\text{N}(\text{CH}_2\text{Ph}) \\ \text{CO} \text{---} \text{C}(\text{OEt}) \end{array} \text{CH}$ , m. p. 163—164°, crystallises in prisms or plates, and does not give a coloration with diazobenzenesulphonic acid. 5-Hydroxy-3-benzyluracil (3-benzylisobarbituric acid), m. p. 200—210°, forms irregular crystals.

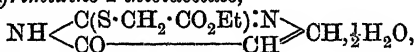
When 5-hydroxy-1-benzyluracil is treated with bromine water at 0°, 1-benzylisodialuric acid,  $\text{CH}_2\text{Ph}\cdot\text{N} \begin{array}{c} \text{CO} \text{---} \text{NH} \\ \text{CO}\cdot\text{C}(\text{OH}) \end{array} \text{C}\cdot\text{OH}$ , m. p. 139° (decomp.), is produced, which forms prismatic crystals and gives a violet barium salt. E. G.

**Pyrimidines.** XL. Thio-derivatives of Uracil and the Preparation of Uracil in Quantity. HENRY L. WHEELER and LEONARD M. LIDDLE (*Amer. Chem. J.*, 1908, 40, 547—558).—In an earlier paper (Wheeler and Merriam, Abstr., 1903, i, 525) a method has been described for the preparation of uracil, depending on the condensation of ethyl sodioformylacetate with  $\psi$ -ethylthiocarbamide and the hydrolysis of the product. It is now found that larger yields can be obtained by using thiocarbamide instead of  $\psi$ -ethylthiocarbamide.

2-Thiouracil,  $\text{NH} \begin{array}{c} \text{CS}\cdot\text{NH} \\ \text{CO}\cdot\text{CH} \end{array} \text{CH}$ , m. p. 340° (decomp.), which is formed in this reaction, crystallises in prismatic plates, and is soluble

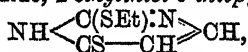
to the extent of 0.0598 gram in 100 parts of water at 17°. 6-Oxy-2-methylthiopyrimidine and 6-oxy-2-ethylthiopyrimidine dissolve to the extent of 0.6620 gram and 0.7930 gram respectively in 100 parts of water at 17°. 2-Thiouracil is a much stronger acid than uracil, and forms crystalline *sodium* and *potassium* salts; the *ammonium*, *mercuric*, and *copper* salts have also been prepared. When 2-thiouracil is boiled with an aqueous solution of chloroacetic acid, a nearly quantitative yield of uracil is obtained. A yield amounting to 66% of the calculated quantity was obtained in a similar manner from 6-thiouracil.

*Ethyl 6-oxypyrimidine-2-thiolacetate*,



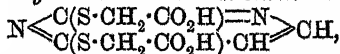
m. p. 154—155°, prepared by the action of ethyl chloroacetate on 2-thiouracil, forms long, lustrous plates. The corresponding *acid*, m. p. 178°, crystallises in prisms with 1H<sub>2</sub>O. By the action of sodium ethoxide and ethyl iodide on 2-thiouracil, 6-oxy-2-ethylthiopyrimidine (Wheeler and Merriam, *loc cit.*) is produced. 6-Oxy-2-benzylthiopyrimidine,  $\text{NH} \begin{array}{c} \text{C}(\text{S} \cdot \text{CH}_2\text{Ph}) \cdot \text{N} \\ \text{CO} \quad \quad \quad \text{CH} \end{array} \text{CH} = \text{CH}$ , m. p. 192—193°,

obtained by the action of benzyl chloride on 2-thiouracil in presence of potassium hydroxide, forms slender prisms, and is soluble in about 16 parts of hot alcohol and in 50 parts of cold; the *sodium* salt crystallises in plates. When 6-chloro-2-ethylthiopyrimidine (Wheeler and Johnson, *Abstr.*, 1903, i, 526) is boiled with an alcoholic solution of potassium hydrosulphide, 2-ethylthiol-6-thiopyrimidine,



m. p. 149°, is obtained, which crystallises in prisms, and, when heated with concentrated hydrochloric acid, is converted into 6-thiouracil,  $\text{NH} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CS} \cdot \text{CH} \end{array} \text{CH} = \text{CH}$ , m. p. 328° (decomp.), which forms light yellow needles.

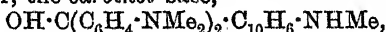
2:6-Dithiouracil,  $\text{NH} \begin{array}{c} \text{CS} \cdot \text{NH} \\ \text{CS} \cdot \text{CH} \end{array} \text{CH} = \text{CH}$ , obtained by heating 2:6-dichloropyrimidine with potassium hydrosulphide, forms bright yellow needles, and decomposes above 230°. This compound is also produced when 2-ethylthiol-6-thiopyrimidine is treated at 170° with dry hydrogen chloride. *Pyrimidine-2:6-dithiolacetic acid*,



obtained by the action of chloroacetic acid on 2:6-dithiouracil, forms a white, crystalline powder, and decomposes above 200°. E. G.

Colour Bases of Triphenylmethane Dyes. II. EMILIO NOELTING and K. PHILIPP (*Ber.*, 1908, 41, 3908—3911. Compare *Abstr.*, 1908, i, 295).—A continuation of former work. Pentamethyl-triaminodiphenyl-naphthylcarbinol hydrochloride, when dissolved in hot water and acetic acid and treated with sodium hydroxide, yields the *imino*-base,  $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{NMe}$ , crystallising in reddish-brown

leaflets, m. p. 195—196°; when the dye is boiled with excess of ammonia, however, the *carbinol* base,



is obtained as colourless crystals, m. p. 171—172°. When heated in glycerol with the addition of a few drops of aqueous potassium hydroxide, the imino-base is formed, and this is again converted into the carbinol when its solution in 40—50% alcohol, to which a little ammonia or potassium hydroxide is added, is boiled for an hour.

When a cold solution of crystal-violet is mixed with a large excess of potassium hydroxide and immediately extracted with ether, reddish-brown crystals, m. p. 191—194°, of the imino-base are obtained. This is soon converted in a vacuum desiccator into the carbinol form, m. p. 182°, which is also formed when a solution of crystal-violet is treated with ammonia. In the case of malachite-green, ammonia decolorises the solution much more quickly than do potassium or sodium hydroxides, but the coloured base could not be obtained pure, owing to its rapid change into the carbinol form.

When *o*-chloromalachite-green (setoglaurin) is treated in aqueous solution with ammonia, the *carbinol* base,  $\text{C}_{23}\text{H}_{25}\text{ON}_2\text{Cl}$ , is obtained; this forms pale yellow crystals, m. p. 155°. By the addition of potassium hydroxide to setoglaurin, a red precipitate is obtained. Further experiments in the preparation of this coloured base are in progress. With sodium methoxide, setoglaurin furnishes the *methyl ether*,  $\text{OMe}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2\cdot\text{C}_6\text{H}_4\text{Cl}$ , pale yellow crystals, m. p. 138°.

J. C. C.

**Chromoisomerism and Transformation of 4-Oximino-1-phenyl-5-triazolone.** OTTO DIMROTH and OSKAR DIENSTRACH (*Ber.*, 1908, 41, 4055—4068).—In connexion with 4-isonitroso-1-phenyl-5-triazolone (Dimroth and Taub, *Abstr.*, 1907, i, 96), two points of interest are discussed, the colour phenomena of the metallic salts and the hydrolysis of its acylated derivatives.

Three series, yellow, green, and red, of metallic salts have been obtained. The only member of the yellow series is the *potassium hydrogen* salt,  $\text{KH}(\text{C}_8\text{H}_5\text{O}_2\text{N}_4)_2\cdot 3\text{H}_2\text{O}$ , which forms yellow, micro-crystalline needles, decomposes at 80—100°, and is obtained by treating the dipotassium salt of 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylic acid with potassium nitrite and acetic acid in the cold. It dissolves unchanged in alcohol or acetone, but after some time the solution contains oximinophenyltriazolone, and a precipitate is obtained of the bluish-green *potassium* salt,  $\text{C}_8\text{H}_5\text{O}_2\text{N}_4\text{K}$ , which is also formed from alcoholic potassium acetate and dilute alcoholic oximinophenyltriazolone. Other metallic salts have been obtained in a similar manner. The *sodium*, *ammonium*, *calcium*, *barium*, and *mercurous* salts belong to the red series. The *silver* salt, prepared from the sodium salt and silver nitrate, or from the oximinophenyltriazolone and silver nitrate in alcoholic solution, separates at the ordinary temperature as a canary-green powder (stable form), and at 50° as a brownish-red labile form, changing to the stable form by cooling.

Acyl derivatives of oximinophenyltriazolone, prepared from the silver salt and acyl chlorides in dry ether, have, in a few cases, been

obtained in yellow and red forms, but not in the green. 4-Benzoyloximino-1-phenyl-5-triazolone,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{N} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{OBz} \end{smallmatrix}$ , separates from alcohol in long, red needles by slow cooling, or in yellow, micro-crystalline needles by rapid cooling. Both forms behave alike, have m. p. 132—133° (decomp.), and give the same yellow solution in organic solvents at the ordinary temperature, but that they are isomeric and not polymorphic is proved by the fact that the red modification in chloroform at 0° gives a blood-red solution, the colour of which changes, however, almost instantly to yellow. When the red modification under alcohol is inoculated with a trace of the yellow isomeride, the whole mass becomes yellow in a few days. The *m*-nitrobenzoyl derivative, m. p. 153°, only occurs in yellow needles. The acetyl derivative is obtained in yellow and red modifications, the separation of the two being difficult; the former has m. p. 97—98°. Phenylcarbimide and oximinophenyltriazolone in ether yield, as the

main product, a phenylurethane,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{N} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh} \end{smallmatrix}$ , m. p. 110° (decomp.), which separates in orange-yellow needles. This compound and the preceding acetyl derivative are hydrolysed by alcoholic potassium acetate, the bluish-green potassium salt of oximinophenyltriazolone being obtained. The benzoyl and the *m*-nitrobenzoyl derivatives are stable to potassium acetate, but their interaction with 5*N*-sodium hydroxide at -10°, the reaction being completed at the ordinary temperature, leads to the formation of benzoic (or *m*-nitrobenzoic) acid and Bladin's 1-phenyl-1:2:3:5-tetrazole-4-carboxylic acid (Abstr., 1886, 146), the identity being confirmed by heating the acid at 140—155°, whereby 1-phenyl-1:2:3:5-tetrazole is obtained. Several explanations are discussed to account for the formation of the tetrazole from the triazole. It appears that, in addition to the two types of the Beckmann transformation already recognised (Werner and Pignet, Abstr., 1905, i, 66; Diels and Stern, Abstr., 1907, i, 480), a third type is possible, in which the acylated hydroxyl group attached to the nitrogen atom exchanges places with a group

attached to the  $\beta$ -carbon atom, thus  $\begin{smallmatrix} \text{R} \cdot \text{C} \cdot \text{C} \cdot \\ \diagup \quad \diagdown \\ \text{OAc} \cdot \text{N} \end{smallmatrix} \rightarrow \begin{smallmatrix} \text{OAc} \cdot \text{C} \cdot \text{C} \cdot \\ \diagup \quad \diagdown \\ \text{R} \cdot \text{N} \end{smallmatrix}$ .

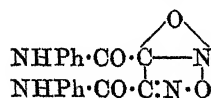
In the case in question:  $\begin{smallmatrix} \text{N} \cdot \text{N} \cdot \text{NPh} \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{OBz} \cdot \text{N} \end{smallmatrix} \rightarrow \begin{smallmatrix} \text{OBz} \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{N} \cdot \text{N} \cdot \text{NPh} \cdot \text{N} \end{smallmatrix} \text{C}$ ,

from which benzoic acid and the tetrazole derivative are obtained.

The benzoyl derivative, m. p. 169—170°, and the *m*-nitrobenzoyl derivative, m. p. 194°, of 4-oximino-1-phenyl-3-methylpyrazolone do not suffer the preceding change, being stable to cold aqueous sodium hydroxide, and hydrolysed normally by sodium ethoxide. C. S.

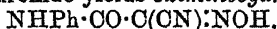
Decomposition Products of 4-Oximino-1-phenyl-5-triazolone. OTTO DIMROTH and OSKAR DIENSTBACH (*Ber.*, 1908, 41, 4068—4083. Compare Dimroth and Taub, Abstr., 1907, i, 96; preceding abstract).—It has already been shown that the decomposition of 4-oximino-1-phenyl-5-triazolone by warm water, or, better, by warm dilute

sulphuric acid, yields nitrogen, oxanilhydroxamic acid, and in addition, two isomeric substances,  $C_{16}H_{12}O_4N_4$ , m. p.  $187^\circ$  and  $195^\circ$  respectively, the constitutions of which were undetermined. The suggestion that the substance, m. p.  $187^\circ$ , is glyoximeperoxidedicarboxyanilide has been substantiated, but, since in the meantime the authors have accepted Wieland and Semper's bridged-ring formula for glyoxime-



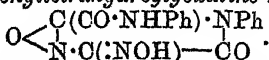
peroxide and its derivatives (Abstr., 1908, i, 108), the name of the substance has been altered to 2:3-endoxy-2:3-dihydrofurazan-3:4-dicarboxyanilide (furoxandicarboxyanilide), and its formula to the annexed constitution. It is reduced by stannous chloride and hydrogen chloride in glacial acetic acid to

*furazan-3:4-dicarboxyanilide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{C} \cdot \text{N} > \text{O}$ , m. p.  $119^\circ$ , the decomposition of which by aqueous sodium hydroxide or methyl alcoholic potassium hydroxide yields *oximinocyanouacetanilide*,

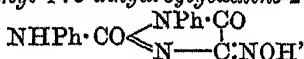


m. p.  $220^\circ$  (decomp.), which forms yellow and colourless crystals, and can be synthesised by heating oxanilhydroxamyl chloride dissolved in ether with silver cyanide at  $100^\circ$  for sixteen hours.

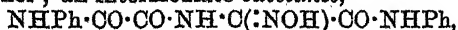
The substance, m. p.  $195^\circ$ , previously regarded as 3:6-dioximino-2:5-diketo-1:4-diphenylpiperazine (*loc. cit.*), is proved to be 4-oximino-2:3-endoxy-5-keto-1-phenyltetrahydroglyoxaline-2-carboxyanilide,



This constitution readily accounts for the formation of oxanilhydroxamic anilide and oxalohydroxamic acid by the action of cold 10% sodium hydroxide [Lossen, Behrend, and Schäfer's sodium oxalohydroxamate (Abstr., 1894, i, 358) is really sodium oxalodihydroxamate], and is in harmony with the behaviour of the substance by reduction by stannous chloride and hydrogen chloride in glacial acetic acid, by phenylhydrazine, or by alcoholic hydrogen chloride, whereby 4-oximino-5-keto-1-phenyl-4:5-dihydroglyoxaline-2-carboxyanilide,



m. p.  $237^\circ$ , is obtained. This compound, which is also prepared from 4-oximino-1-phenyl-5-triazolone, methyl alcohol, and concentrated hydrochloric acid, from the potassium hydrogen salt of the triazolone derivative and alcohol, or from the sodium salt and alcoholic sodium acetate, is decomposed by methyl alcoholic potassium hydroxide, yielding oxanilic acid and *oxanilhydroxamamide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{C}(\text{NOH}) \cdot \text{NH}_2$ , m. p.  $142^\circ$ , which forms a compound, m. p.  $175^\circ$ , with phenylcarbimide, and is synthesised from ammonia and oxanilhydroxamic chloride in moist ether. The constitution of the dihydroglyoxaline derivative is also proved by synthesis from oxanilyl chloride and oxanilhydroxamamide in ether; an intermediate substance,



m. p.  $181-183^\circ$ , is formed, which crystallises in colourless needles or rhombic leaflets, and loses 1 mol.  $H_2O$  above its m. p., yielding 4-oximino-5-keto-1-phenyl-4:5-dihydroglyoxaline-2-carboxyanilide.

The conversion of the endoxyglyoxaline derivative, m. p. 195°, into the endoxydihydrofuran, m. p. 187°, is accomplished (a) by dilute sodium hydroxide, (b) by the action of benzoyl chloride in pyridine, (c) by the prolonged shaking of its solution in ether or acetone half saturated with hydrogen chloride. When ether, saturated with hydrogen chloride at 5°, is used, the endoxyglyoxaline derivative is decomposed, ammonia, aniline, oxalic acid, phenyloxamide, and oxanilhydroxamamide being formed.

C. S.

**Azinpurines.** FRANZ SACHS and GEORG MEYERHEIM (*Ber.*, 1908, 41, 3957—3965).—Whereas the purine compounds have been extensively examined, compounds analogous, but containing one more carbon atom in the nucleus, are almost unknown. The azinpurines may be obtained by the condensation of 4:5-diaminopyrimidines with *o*-diketones.

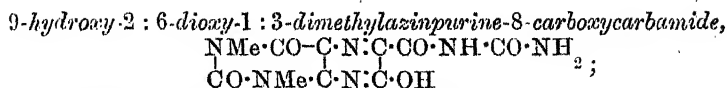
2:6-Dioxy-3:8:9-trimethylazinpurine, 
$$\begin{array}{c} \text{NH} \cdot \text{CO} - \text{C} \cdot \text{N} : \text{CMe} \\ | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} : \text{CMe} \end{array}$$
 obtained from 4:5-diamino-2:6-dioxy-3-methylpyrimidine and diacetyl in 93% yield, crystallises from water in small needles, m. p. 328—330°; its aqueous solution is yellow with a green fluorescence. 2:6-Dioxy-1:3:8:9-tetramethylazinpurine,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_4$ , from 4:5-diamino-2:6-dioxy-1:3-dimethylpyrimidine, is obtained in 84% yield, and crystallises in needles, m. p. 159.5°.

2:6-Dioxy-8-acetyl-3:9-dimethylazinpurine, 
$$\begin{array}{c} \text{NH} \cdot \text{CO} - \text{C} \cdot \text{N} : \text{CAc} \\ | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} : \text{CMe} \end{array}$$
 obtained by the condensation of the monomethyl base with triketopentane in aqueous acetic acid solution, crystallises from water in prisms, m. p. 267°; the solution is colourless. Condensation with the dimethyl base and triketopentane leads to the formation of 2:6-dioxy-8-acetyl-1:3:9-trimethylazinpurine,  $\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_4$ , which crystallises from alcohol in long needles, m. p. 164—165°.

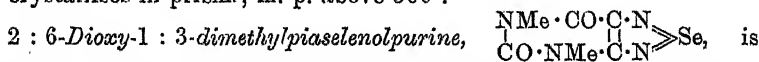
9-Hydroxy-2:6-dioxy-3:8-dimethylazinpurine, 
$$\begin{array}{c} \text{NH} \cdot \text{CO} - \text{C} \cdot \text{N} : \text{CMe} \\ | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{OH} \end{array}$$
 from monomethyl base and pyruvic acid, is purified by dissolution in aqueous ammonia and precipitation with dilute hydrochloric acid; m. p. 323—324°. The 9-hydroxy-2:6-dioxy-1:3:8-trimethylazinpurine,  $\text{C}_9\text{H}_{10}\text{O}_3\text{N}_4$ , from the dimethyl base, crystallises from formic acid, has m. p. 309°, and gives a yellowish-red lead, an orange silver, a yellow barium, and a yellowish-red copper salt.

9-Hydroxy-2:6-dioxy-1:3-dimethylazinpurine,  $\text{C}_8\text{H}_8\text{O}_3\text{N}_4$ , from the dimethyl base and ethyl dichloroacetate, separates from alcohol as a white compound, m. p. 282°. 9-Hydroxy-2:6-dioxy-1:3-dimethylazinpurine-8-carboxylic acid, 
$$\begin{array}{c} \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{CO} \cdot \text{NMe} \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{OH} \end{array}$$
 obtained from mesoxalic acid and dimethyl base in 67% yield, crystallises in slender needles from water, m. p. 239—240° (decomp.).

Condensation of alloxan and dimethyl base leads to the formation of



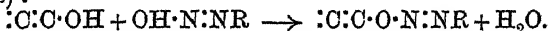
it crystallises in prisms, m. p. above  $360^\circ$ .



formed when an acetic acid solution of the dimethyl base is treated with selenious acid; it is brick-red in colour, m. p.  $225-230^\circ$ . The colour is destroyed on solution in water, from which it crystallises in long, colourless, prismatic needles, m. p.  $227-228^\circ$ .

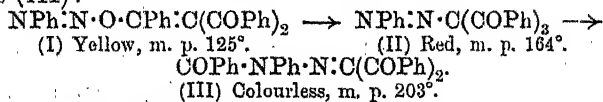
[With W. BRUNETTI.]—2-Amino-6-hydroxy-8 : 9-dimethylazainpurine,  $\text{N} : \text{C}(\text{OH}) - \text{C} \cdot \text{N} : \text{CMe} \cdot \text{C}(\text{NH}_2) \cdot \text{N} \cdot \text{C} \cdot \text{N} : \text{CMe}$ , formed by the condensation of 2 : 4 : 5-triamino-6-hydroxypyrimidine sulphate with diacetyl in aqueous solution, crystallises in small, yellow needles, which sublime without melting. It forms a yellow *picrate* and a *silver salt*,  $\text{C}_8\text{H}_5\text{ON}_5\text{Ag}$ . W. R.

**The Mechanism of Coupling.** OTTO DIMROTH and MAX HARTMANN (*Ber.*, 1908, 41, 4012-4028).—It has been shown previously (*Abstr.*, 1907, i, 662, 1090) that only the enolic forms of keto-enolic tautomerides react with diazo-compounds. It is now shown that the first stage in this reaction consists in the formation of an azo-compound in which the azo-group is attached to oxygen (*O*-azo-compounds):



The constitution of these compounds follows from their behaviour. When boiled with alcohol they react as diazo-ethers; thus benzene-*O*-azotribenzoylmethane, obtained from diazobenzene and tribenzoylmethane, decomposes into tribenzoylmethane and benzene, whilst the alcohol is oxidised to aldehydes. They also react with phenols and amines in the same manner as diazo-ethers, for example, benzene-*O*-azotribenzoylmethane reacts with an alcoholic solution of  $\beta$ -naphthol, yielding tribenzoylmethane and benzeneazo- $\beta$ -naphthol. Similarly, the *O*-azo-compound is decomposed by an ethereal solution of hydrogen chloride, yielding diazobenzene chloride and tribenzoylmethane.

When the yellow *O*-azo-compound is kept at a temperature just above its melting point, it is transformed into a red isomeric compound (II), and when this is further heated it sets to a mass of colourless crystals (III):



The red compound has been identified as a *C*-azo-compound, owing to its stability; it does not react with amines or phenols, and is not hydrolysed by ethereal hydrogen chloride, but merely transformed more quickly into the colourless compound (III). When reduced it yields a leuco-compound, namely, a hydrazo-compound, which readily oxidised back to the red azo-compound. The colourless hydrazone (III) is also stable; it does not couple with phenols or

amines, and on reduction yields benzanilide. All three compounds react with sodium ethoxide, yielding ethyl benzoate and diphenyltriketone phenylhydrazone,  $\text{C}(\text{COPh})_3 \cdot \text{N} \cdot \text{NHPh}$ , m. p. 153—154°. The "coupling" of a phenol with a diazo-compound is also regarded as primarily consisting in the formation of an *O*-azo-derivative,  $\text{PhO} \cdot \text{N} \cdot \text{N} \cdot \text{Ph}$ , which undergoes molecular rearrangement to the more stable hydroxyazo-derivative (compare Kekulé, *Ber.*, 1870, 3, 233). An *O*-azo-compound of this type has been isolated by coupling *p*-bromodiazobenzene chloride with *p*-nitrophenol. It is practically colourless, and when heated at 80° yields the more stable *C*-azo-compound,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4(\text{OH}) \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$ .

*Benzene-O-azotribenzoylmethane* (I) separates from its ethereal or chloroform solution on the addition of light petroleum as long, canary-yellow prisms, m. p. 125°.

*Benzene-C-azotribenzoylmethane* (II) is best obtained by heating the *O*-compound under reduced pressure at 100° for about two hours; it can be separated from the colourless hydrazone (III), which is also formed by extraction with ether and fractional crystallisation from acetone. It forms glistening, hard prisms of a ruby-red colour, melts at 164°, and at the same time is rapidly transformed into the colourless *benzoylphenylhydrazone* of *diphenyltriketone* (III), which crystallises from benzene in colourless needles, m. p. 203°.

The compound previously described as *p*-bromobenzeneazotribenzoylmethane (Abstr., 1907, i, 1090) is now shown to be the isomeric *O*-azo-derivative. It is rapidly transformed into the isomeric *C*-azo-compound, but this cannot be isolated, as it is immediately converted into the hydrazone (*loc. cit.*). *Diphenyl triketone bromophenylhydrazone* (*p*-bromobenzeneazodibenzoylmethane),  $\text{C}_{21}\text{H}_{15}\text{O}_3\text{N}_2\text{Br}$ , is formed by the action of sodium ethoxide on either the *O*-azo-compound or its isomeride. It crystallises from alcohol in golden-yellow plates, m. p. 147—149°.

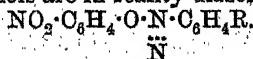
The properties of the compound previously described as benzene-azoacetyldibenzoylmethane prove that it is an *O*-azo-compound; similarly, Bülow and Hailer's ethyl phenylazodibenzoylacetate (Abstr., 1902, i, 327) is an *O*-azo-compound, although it cannot be transformed into a more stable isomeride.

Ethyl benzoylmalonate reacts with diazobenzene chloride, yielding *ethyl benzene-O-azobenzoylmalonate*,  $\text{N}_2\text{Ph} \cdot \text{O} \cdot \text{CPh} \cdot \text{C}(\text{CO}_2\text{Et})_2$ , which crystallises from alcohol in glistening, yellow plates, m. p. 69°; when heated slightly above its m. p., it is completely decomposed.

*Benzene-O-azo-p-nitrophenol*,  $\text{N}_2\text{Ph} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , has been obtained in the form of pale yellow needles, which rapidly decompose. *p*-Bromobenzene-*O*-azo-*p*-nitrophenol,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{N}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , melts at 75—80°, and is also unstable; at 80° it is transformed into the isomeric *p*-bromobenzeneazo-*p*-nitrophenol,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NO}_2$ , m. p. 197°.

J. J. S.

*O*-Azo-compounds. KARL AUWERS (*Ber.*, 1908, 41, 4304—4308. Compare Dimroth and Hartmann, preceding abstract).—It is suggested that the relatively unstable *O*-azo-compounds prepared from diazotised *p*-nitroaniline and phenols are in reality diazonium salts,

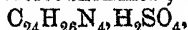


Similar compounds are obtained when diazonium salts react with phenols, the ortho-para-positions of which are occupied. The radicles need not be negative in character, as mesitol gives the reaction, although with difficulty. The compounds so obtained are more stable than those of Dimroth and Hartmann, which may be due to the fact that they cannot be transformed into hydroxyazo-compounds.

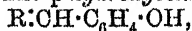
W. R.

**Condensation of 2:3'-Dimethylazobenzene-4-hydrazine-sulphonic Acid**, formed by the Action of Sulphurous Acid on Diazo-*m*-toluene Sulphate, with Aldehydes and Ketones. JULIUS TRÖGER and GEORG PUTTKAMMER (*J. pr. Chem.*, 1908, [ii], 78, 437—449. Compare Abstr., 1907, i, 263).—A continuation of the investigations of Tröger, Warnecke, and Schaub (Abstr., 1906, i, 993). 2:3'-Dimethylazobenzene-4-hydrazinesulphonic acid condenses with aldehydes and ketones in alcoholic solution containing hydrogen chloride or sulphuric acid, with elimination of the sulphonic group, yielding derivatives of 2:3'-dimethylazobenzene-4-hydrazone hydrochloride or sulphate. The free hydrazones are obtained by treating the salts with ammonium hydroxide. The following hydrazones were prepared in this way. In the formulæ  $R = C_6H_4Me \cdot N : N \cdot C_6H_3Me \cdot NH \cdot N$ . All the salts described were analysed (see following abstract).

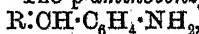
*p*-Tolylidene-2:3'-dimethylazobenzene-4-hydrazone,  $R : CH \cdot C_6H_4Me$ , crystallises in yellow leaflets, m. p. 180—181°; the *hydrochloride*,  $C_{22}H_{22}N_4 \cdot HCl$ , is a sandy, crystalline, violet powder. The corresponding *p*-isopropylbenzylidene derivative,  $R : CH \cdot C_6H_4Pr^s$ , forms stellate groups of brown crystals, m. p. 137°; the *hydrochloride* is a dark reddish violet, crystalline powder; the *hydrobromide*,  $C_{24}H_{26}N_4 \cdot HBr$ , is a black, crystalline powder with a violet shimmer; the *sulphate*,



is amorphous. The *m*-chlorobenzylidene derivative,  $R : CH \cdot C_6H_4Cl$ , forms pale orange, silky crystals, m. p. 140°; the *hydrochloride* crystallises in slender, violet needles. The *m*-bromobenzylidene derivative,  $R : CH \cdot C_6H_4Br$ , crystallises in pale orange leaflets, m. p. 137°; the *hydrobromide* forms dark violet needles; the *sulphate* crystallises in bronze-green needles. The *p*-hydroxybenzylidene derivative,



crystallises in brown leaflets, m. p. 202—203°; the *hydrochloride* forms bluish-green needles; the *hydrobromide* forms green needles; the *sulphate* crystallises in dark blue needles. The *p*-dimethylaminobenzylidene derivative,  $R : CH \cdot C_6H_4 \cdot NMe_2$ , is an orange powder, m. p. 154—155° (decomp.); the *hydrobromide*,  $C_{28}H_{28}N_5 \cdot 2HBr$ , is a brownish-black, crystalline powder. The *p*-aminobenzylidene derivative,



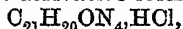
is an amorphous, orange powder, m. p. 188—190° (decomp.); the *hydrochloride*, a bronze-green powder, appears to contain 2 mols. of hydrogen chloride. The benzophenone condensation product,  $R : CPh_2$ , crystallises in reddish-orange, microscopical prisms, m. p. 137°; the corresponding isopropylidene derivative,  $R : CMe_2$ , forms small, brown, flat, oval crystals, m. p. 125°; the *hydrochloride* is a brownish-red,

crystalline powder; the *benzil* derivative,  $R \cdot CPh \cdot CPh \cdot R$ , crystallises in orange, rectangular plates, m. p. 141—142°. W. H. G.

**Additive Products of 2:3'-Dimethylazobenzene-4-hydrazones with Acids.** JULIUS TRÖGER and GEORG PUTTKAMMER (*J. pr. Chem.*, 1908, [ii], 78, 450—477. Compare preceding abstract).—It is definitely shown in this communication that when 2:3'-dimethylazobenzene-4-hydrazinesulphonic acid condenses with aldehydes or ketones in the presence of strong mineral acids, only hydrazone salts are formed. The statement of Tröger, Hille, and Vasterling (*Abstr.*, 1906, i, 120), that the sulphonic acid condenses with salicylaldehyde, thus:  $OH \cdot C_6H_4 \cdot CHO + 2C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_3H_2 \cdot SO_3H + H_2O = 2H_2SO_4 + OH \cdot C_6H_4 \cdot CH(C_7H_6 \cdot N_2 \cdot C_7H_6 \cdot NH \cdot NH_2)_2$ , is incorrect. The salts described in this paper, descriptions of many of which have been given in the preceding abstract in order to economise space, are obtained in a pure state only by using exceedingly pure materials, and by the following methods: (1) heating the sulphonic acid in alcohol, or, better, glacial acetic acid, with an aldehyde or ketone in the presence of a mineral acid; (2) treating the pure hydrazone with a solution of the mineral acid in glacial acetic acid. Unless otherwise stated, all the salts are composed of 1 mol. of the hydrazone with 1 mol. of acid.

*Benzylidene-2:3'-dimethylazobenzene-4-hydrazone hydrochloride*,  $C_{21}H_{20}N_4 \cdot HCl$ , forms dark violet needles; the *hydrobromide* forms black needles with violet reflex; the *sulphate* forms blue crystals.

The *o*-hydroxybenzylidene derivative forms a *hydrochloride*,



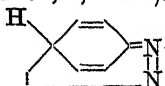
small, dark green needles; *hydrobromide*, brownish-black, crystalline powder, and *sulphate*, small, green needles. The *m*-nitrobenzylidene derivative forms a *sulphate*,  $C_{21}H_{19}O_2N_5 \cdot H_2SO_4$ , green crystals; *hydrochloride*, slender, dark green needles, and *hydrobromide*, slender, microscopical, reddish-violet needles. The analogous *p*-nitro-compound yields a *hydrochloride*, bluish-violet needles, and *sulphate*, deep green needles. The *hydrochloride*, *hydrobromide*, and *sulphate* of the *p*-methoxybenzylidene derivative are blue, crystalline substances. *Cinnamylidene-2:3'-dimethylazobenzene-4-hydrazone hydrochloride*,  $C_{28}H_{22}N_4 \cdot HCl$ , crystallises in greyish-blue needles; the *hydrobromide* forms brownish-black needles; the *sulphate* forms slender, bronze-green needles; the *hydriodide* is a bluish-black, crystalline powder. W. H. G.

**Preparation of *o*-Azocarboxylic Acids.** PAUL FREUNDLER and SEVESTRE (*Compt. rend.*, 1908, 147, 981—983).—The *o*-azo-carboxylic acids required for the preparation of 3-hydroxyindazyl derivatives (*Abstr.*, 1906, i, 544; 1907, i, 158), and prepared by the condensation of nitrosobenzene with the meta-substituted anthranilic acid, can be obtained in a far better yield by the condensation of the primary aromatic amine with the *o*-nitroso-acid; thus *p*-chloroaniline and *o*-nitrosobenzoic acid yield *p*-chlorobenzene-*o*-azobenzoic acid to the extent of 60% of that required by theory, whilst the yield by the older method is only 15%, and the following compounds were similarly prepared: *p*-toluene-*m*-azotoluic acid forms large, red prisms, m. p. 122·5°; *p*-toluene-2-azo-5-chlorobenzoic acid crystallises in orange plates, m. p. 159—160°.

The *o*-nitroso-acids required in these preparations were obtained by oxidising the corresponding amino-acid with Caro's acid (compare Baeyer, Abstr., 1900, i, 206); *o*-nitroso-*m*-toluic acid forms small, yellow prisms, m. p. 172—173°; 5-chloro-2-nitrosobenzoic acid crystallises in plates, m. p. 193°. M. A. W.

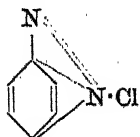
**Decomposition of Diazo-solutions.** JOHN C. CAIN (*Ber.*, 1908, 41, 4186—4189).—It is pointed out by the author that the value given by Hantzsch and Thompson (Abstr., 1908, i, 1021) for the rate of decomposition of a solution of pure *p*-nitrodiazobenzene chloride at 50° ( $K=0.00020$ ) is in close agreement with that calculated for 50° ( $K=0.00018$ ) from the result obtained by him (Trans., 1902, 81, 1436) for the rate of decomposition of a solution of the same compound containing a trace of free nitrous acid (about 0.0003 gram in 70 c.c.) at 80° ( $K=0.00736$ ). The statement made by the author previously, that the very small quantity of nitrous acid present in a diazo-solution prepared by the usual method does not appear to exert any influence on the rate of decomposition of the solution, is thus shown to be correct. W. H. G.

**Theory of Diazo-compounds and Ammonium Salts.** JOHN C. CAIN (*Ber.*, 1908, 41, 4189—4193).—Polemical. A reply to the criticisms of Hantzsch (Abstr., 1908, i, 1021). The objection

that a compound having the formula  would yield

*p*-phenylenediamine on reduction has already been answered (Proc., 1907, 23, 160). The equation representing the dissociation of tetraethylammonium chloride in aqueous solution should be  $\text{NEt}_4\cdot\text{Cl}\cdot\text{Et} \rightarrow \text{NEt}_3 + \text{Cl}' + \text{Et}' \rightarrow \text{NEt}_4^+ + \text{Cl}'^-$ ; that is, the formation of the ion  $\text{NEt}_4^+$  can take place momentarily without the separate formation of ethyl chloride. W. H. G.

**Constitution of Diazonium Salts.** HANS EULER (*Ber.*, 1908, 41, 3979—3981).—In connexion with Hantzsch's criticisms (Abstr., 1908, i, 1021) of Cain's formula (Trans., 1907, 91, 1049), the author points out that, in 1906, he suggested the annexed formula, which has an advantage over other formulae in that it pictorially represents the ability of aromatic, as against the inability of aliphatic and alicyclic, amines to yield diazonium salts, and the transformation of diazonium salts into *syn*-diazo-oxides, whilst it is not in discord with the chemical and electrochemical behaviour of these substances. C. S.



**Dimethylaminoazoantipyrene.** FRIEDRICH STOLZ (*Ber.*, 1908, 41, 3849—3854).—The method for preparing 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone recently patented by the "Société chimique de l'Avanchet" (D.R.-P. 203753) must be wrong, since nitrosodimethylamine and 4-aminoantipyrene do not interact under the conditions mentioned in the patent. Dimethylaminoazoantipyrene may,

however, be readily prepared by coupling dimethylamine with diazo-antipyrine, but when heated, it does not yield 4-dimethylaminoantipyrine, but passes into 1-phenyl-2-methyl-3:4-pyrazopyrazol-5-one with elimination of dimethylamine.

*Diethylaminoazoantipyrine*,  $C_{15}H_{21}ON_5$ , crystallises in light brown prisms, m. p. 111—112°.

*Dimethylaminoazoantipyrine*,  $C_{13}H_{17}ON_5$ , crystallises in brownish-yellow leaflets, m. p. 107° (heated rapidly), 110—112° (heated slowly). It is converted when heated at 130—140°, or more readily when its solution in xylene is boiled, into 1-phenyl-2-methyl-3:4-pyrazopyrazol-5-

one,  $NPh \begin{array}{c} \text{NMe} \cdot \text{C} : \text{CH} \\ \diagup \quad \diagdown \\ \text{CO} - \text{C} = \text{N} \end{array} \text{NH}$ , which forms small, orange crystals, m. p. 173°, and yields an *acetyl* derivative,  $C_{13}H_{15}O_2N_4$ , almost colourless crystals, m. p. 202—203°. W. H. G.

**Decomposition Products of Albumin which Combine with Iodine.** HERMANN PAULY and KARL GUNDERMANN (*Ber.*, 1908, 41, 3999—4012. Compare Wheeler and Jamieson, *Abstr.*, 1905, i, 350).

—Indole yields 3-iodoindole,  $C_8H_7 \begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{CH}$ , when a dilute aqueous solution (0.5 gram per litre) is mixed with 10 c.c. of a 10% potassium hydroxide solution and *N*/10 or *N*/100 iodine is run in until a precipitate is no longer formed. The iodo-derivative is deposited as pure crystals, m. p. 72°; with mineral acids, it yields hydrogen iodide. The *picrate*,  $C_8H_6NI, C_6H_3N_3O_7$ , crystallises from alcohol in slender needles, which decompose at 90°. Indole, free from scatole, can be titrated in dilute alkaline solution by means of standard iodine solution. Indole is oxidised to indigo when an *N*/10 iodine solution is added gradually to an indole solution in the presence of a large excess of sodium hydrogen carbonate, but an appreciable amount of 3-iodoindole is always formed as a by-product.

$\alpha$ -Methylindole yields 3-iodo-2-methylindole,  $C_9H_8NI$ , which crystallises in colourless plates, m. p. 82°. It has a strong odour of scatole, and is unstable. The *picrate* crystallises in reddish-brown needles, m. p. 107° (decomp.). Indole derivatives in which the 3-position is already substituted, for example, scatole and dimethylindole, do not yield 3-iodo-compounds. When an aqueous solution of scatole is treated with iodine solution, a small amount of a compound,  $C_9H_9O_2N$  or  $C_9H_{11}O_2N$ , is obtained as a yellow powder, m. p. 140—145°, when slowly heated.

Glyoxaline readily reacts with iodine in the presence of alkali hydroxide, yielding tri-iodoglyoxaline,  $Cl \begin{array}{c} \text{N} - \text{Cl} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{Cl} \end{array}$ , in the form of its

alkali salt. The free acid crystallises from 20% alcohol in large, flat, glistening prisms, m. p. 191—192° (corr.). The *hydrochloride*,  $C_3H_3N_2I_3 \cdot HCl$ , is deposited as glistening needles on the addition of concentrated hydrochloric acid to an alcoholic solution of the glyoxaline. It evolves iodine at 200°, and melts at 220°. When insufficient iodine is used, a di-iodo-derivative, m. p. 180°, is obtained.

Methylglyoxaline (Windaus and Knoop, *Abstr.*, 1905, i, 381) yields

*iodo-2-methylglyoxaline*,  $C_4H_5N_2I$ , in the absence of sodium hydroxide, but the yield is increased by the addition of alkali. The iodo-derivative crystallises from 50% alcohol in colourless needles, m. p. 157°. It is odourless, and forms soluble salts with mineral acids. The *aurichloride*,  $C_4H_5N_2I, HAuCl_4$ , crystallises from hot water in long, orange-yellow needles, m. p. 197°.

Benzimidazole is most readily obtained by heating anhydrous formic acid with *o*-phenylenediamine, and reacts with iodine in the presence of sodium hydroxide, yielding 2-iodobenzimidazole,  $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{Cl}$ , which forms colourless plates, m. p. 187°. It is readily decomposed by acids, but is more stable in the presence of alkalis.

Iminazoles do not yield iodo-derivatives when the hydrogen of the NH-group has been substituted, as in *N*- $\alpha$ -dimethylglyoxaline.

Compounds which are readily iodated in the cold by iodine and alkali are regarded as containing an "iodophore" group. J. J. S.

**Acid and Neutral Copper Albumins.** GIUSEPPE BONAMARTINI and M. LOMBARDI (*Zeitsch. physiol. Chem.*, 1908, 58, 165—174).—When solutions of egg-albumin are mixed with copper sulphate solutions, precipitates of an acid copper albumin are obtained. The mean composition is: albumin, 86.7%; Cu, 5.2%; and  $SO_4$ , 8.0%. The copper and  $SO_4$ -group are practically in the same ratio as in copper sulphate. When a solution of normal potassium hydroxide is added to the precipitate until the liquid is just alkaline, a neutral copper albumin is obtained. This is deeper in colour, and contains no sulphate radicle. If a smaller amount of alkali is used, a mixture of the acid and neutral albumins is obtained. J. J. S.

**Products Formed by the Decomposition of Casein.** I. W. BISSEGER and L. STEGMANN (*Zeitsch. physiol. Chem.*, 1908, 58, 147—152. Compare Winterstein and Thöni, Abstr., 1902, ii, 687).—When casein is digested for some time with pancreatin and pepsin in the presence of toluene and sodium fluoride, tetra- and penta-methylenediamines cannot be isolated, but a new basic substance can be obtained from the lysine fraction. Full details for the isolation of the base are given. The *chloride* crystallises from water in large, glistening, hard prisms, containing 12.5% N and 20.5% Cl. It has  $[\alpha]_D + 11.12^\circ$ , and yields a flocculent precipitate with phosphotungstic acid, and a sparingly soluble *platinichloride* (Pt = 33.51%). J. J. S.

**Different Forms of Nitrogen in Proteins.** THOMAS B. OSBORNE, C. S. LEAVENWORTH, and C. A. BRANTLECHT (*Amer. J. Physiol.*, 1908, 23, 180—200).—It does not appear possible to determine accurately the monoamino-acids in the cleavage products of proteins. Ammonia and the hexone bases can be determined with accuracy, and their estimation by different methods in the same protein gives constant results. It therefore appears that the determination of such substances is a trustworthy criterion in the differentiation of proteins. Hydrolysis must, however, be continued for at least twenty-four hours when dealing with vegetable proteins. Determinations are given in twenty-

six different proteins. The amount of arginine varies from 1% to 14%. Histidine is more constant, 2.5% being present in most proteins. Lysine is absent from the gliadins, and present in leguminous seed-proteins (4–5%), and in con-albumin from hen's egg (over 6%). The oil-seeds contain least arginine, then come the leguminous seed-proteins, and those of cereal grains contain most. W. D. H.

**So-called "Protagon."** OTTO ROSENHEIM and M. CHRISTINE TEBB (*Quart. J. exp. Physiol.*, 1908, 1, 297–304).—Further proofs are advanced that protagon, even when prepared with all the precautions recommended by Wilson and Cramer, is a mixture of different substances. Its composition is completely changed by recrystallisation from alcohol, but the readiest way of separating its constituents is by means of pyridine. Protagon is soluble in this reagent at 30–45°, and a precipitation occurs on cooling; the precipitate consists of the phosphorus-rich constituent (Thudichum's sphingomyelin); the filtrate contains the constituent phrenosin, which is phosphorus-free, and which is precipitable by adding acetone. Their optical activity is different, and the results given fully explain Wilson and Cramer's statements on this subject. Both yield fluid spherocrystals, but the appearances, which are figured, of these are very different in the two cases. W. D. H.

**Kinetics of Enzymes.** SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1908, 57, 468–475).—The velocity of the action of trypsin on caseinogen (the quantity of substrate being constant) is inversely proportional to the amount of the ferment. If white of egg is mixed with the caseinogen, the partition of the ferment between the two proteins is unequal. W. D. H.

**Fermentative Cleavage of Polypeptides.** VI. EMIL ABDERHALDEN and CARL BRAHM (*Zeitsch. physiol. Chem.*, 1908, 57, 342–347. Compare Abstr., 1908, i, 488).—A comparison is made of the action of intestinal juice and yeast juice on *D*-alanyl-glycine and glycyl-*L*-leucine. Both juices act at about the same rate. The same is true for their action on tripeptides, *D*-alanyl-glycyl-glycine being split into *D*-alanine and glycyl-glycine, and glycyl-*D*-alanyl-glycine being split into glycine and *D*-alanyl-glycine. W. D. H.

**Accelerating Influence of Magnesium on Sugar Inversion.** J. TRIBOT (*Compt. rend.*, 1908, 147, 706–707).—Yeast invertase was purified by successive precipitations from aqueous solution by alcohol, and its sacroclastic activity compared with the percentage and composition of the ash. Crude invertase gave 45.76% of ash, of which 1.8% consisted of MgO. In purified invertase, the ash was almost entirely MgO, which gradually diminished from 10.9% to 0.69% on further purification. The activity of the invertase also diminished. It is therefore supposed that magnesium oxide exercises a positive accelerating effect on sugar inversion. R. J. C.

**Action of Colloidal Ferric Hydroxide on Expressed Yeast-juice.** FRIEDRICH RESENSCHECK (*Biochem. Zeitsch.*, 1908, 15, 1—11).—By precipitating yeast-juice with colloidal ferric hydroxide, the former underwent a preliminary loss of fermentative power. The precipitate, when added to fresh yeast-juice, increased its power, and was also capable of reactivating old juice. The iron precipitate contained phosphorus, and other experiments indicated that it contained the co-enzyme. S. B. S.

**Hydrolysis of Amygdalin by Emulsin.** LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1908, 246, 710. Compare Abstr., 1908, i, 817).—A reply to Feist (Abstr., 1908, i, 903), re-stating the author's contention. T. A. H.

**Asymmetric Syntheses by means of Enzyme Action.** LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1908, 14, 238—253).—*d*-Benzaldehydecyanohydrin can be synthesised by the action of emulsin on a mixture of benzaldehyde and 5% hydrocyanic acid.

In the experiments, the mixtures were placed in a shaking machine and kept at a constant temperature. The largest amounts of active cyanohydrin are formed at about 25°, and the optimum is reached after two to three hours. Comparative experiments with and without emulsin show that the emulsin acts as a catalyst, since a much larger percentage of the hydrogen cyanide is fixed during a given time when emulsin is present. The synthetical enzyme is apparently not identical with the hydrolysing enzyme, which is capable of hydrolysing emulsin, since a 2% emulsin solution when heated at 45° during eight days can no longer act on amygdalin, although it is capable of synthesising benzaldehydecyanohydrin to a certain extent. The amount of active cyanohydrin formed tends to increase with the amount of emulsin present, but an excess of hydrogen cyanide has but little effect; the greatest optical effect is produced when a considerable excess of benzaldehyde (more than 1 equivalent) is added slowly to a mixture of emulsin and hydrocyanic acid (less than 1 equivalent).

The mandelic acid obtained by hydrolysing the active nitrile is the pure *l*-acid, with  $[\alpha]_D - 153.78^\circ$ .

Reductases in yeast and milk appear to be able to reduce benzoyl-formic acid to *l*-mandelic acid. J. J. S.

**The Rennet from Decapod Crustaceans.** O. GERBER (*Compt. rend.*, 147, 708—710).—The preparations were made both from gastric juice and by maceration of the hepatic glands. The rennet thus obtained differs from other rennets of animal origin in its resistance to the action of heat and of acids. In this respect it is similar to the rennets of vegetable origin. Neutral salts of alkalis and alkaline earths accelerate the action when in small quantities, but retard it when in larger quantities. S. B. S.

**The Effect of Dialysis on Juices of Vegetable Origin containing Rennet.** O. GERBER (*Compt. rend.*, 1908, 147, 601—603).—The juices from *Ficus Carica* and *Broussonetia papyrifera*

were the subjects of experiment. On submitting them to dialysis, they lost their rennet-like action, and a precipitate formed at the same time. The latter, however, on solution in 5% sodium chloride, exerted a much stronger action than the solution from which it had separated, salt being added to the latter. The rennet-like enzyme appears therefore to be either a globulin or to be carried down with the globulins.

S. B. S.

**Destruction of Rennet by Light.** SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (*Zeitsch. physiol. Chem.*, 1908, 58, 233—254).—The weakening of rennet by light is a unimolecular reaction. The reaction velocity, as in other photochemical reactions, is but little influenced by temperature. The most active rays are those between 220 and 250  $\mu\mu$ ; about 4% of the action is due to rays between 250 and 313  $\mu\mu$ , and about 0.3% to visible rays.

W. D. H.

**Peroxydase Accelerators and their Possible Significance for Biological Oxidations.** JOSEPH H. KASTLE (*Amer. Chem. J.*, 1908, 40, 251—266).—It is well known that, owing to the liability of cows' milk to vary considerably in peroxydase activity, the application of the peroxydase reaction for discriminating between raw and boiled milk is not admissible. Recently, however, Kastle and Porch (*Abstr.*, 1908, ii, 409) have shown that this power of milk to induce the reaction may be greatly intensified by the addition of certain phenols. The author now shows that with some specimens of fresh cows' milk, over thirty times as much phenolphthalein is oxidised in the presence of the three cresols as is oxidised by the milk and hydrogen peroxide alone; and on an average three times as much. With  $\beta$ -naphthol the average is about eight times. In general, the activity of the peroxydase, from whatever source, is found to be greatly increased by phenol, the cresols, and  $\beta$ -naphthol. Tables are given showing the effect of various substances on the peroxydase activity of extracts of horse-radish root, malt, and human saliva. It is suggested that peroxydase accelerators act as auxiliary oxygen carriers, and are themselves oxidised more or less completely by such processes, and are of considerable significance in biological oxidations.

J. V. E.

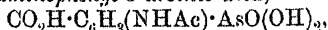
**Hydrogenase or Reductase?** J. GRÜSS (*Ber. Deut. bot. Ges.*, 1908, 26a, 627—630).—The author discusses the reductions effected by the yeast cell, and concludes that they are effected by nascent hydrogen, and are not due to any direct action of a yeast constituent on the substance reduced. This being the case, the enzyme producing the reduction should be called "hydrogenase" and not "reductase."

E. J. R.

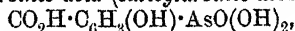
**Some Homologues and Derivatives of Arsanilic Acid. II. Oxidation of Aminotolylarsinic Acids.** ROBERT KAHN and LUDWIG BENDA (*Ber.*, 1908, 41, 3859—3865).—An investigation on the carboxylic acids obtained by oxidising the acetyl derivatives

of the methyl homologues of arsanilic acid (compare Abstr., 1908, i, 591).

*1-Carboxy-6-acetaminophenyl-3-arsinic acid,*



is prepared by oxidising 6-acetaminotolyl-3-arsinic acid in aqueous solution with potassium permanganate; it crystallises in very long, slender, white needles, with  $1\text{H}_2\text{O}$ , m. p. about  $230^\circ$  (decomp.), and when hydrolysed with alkali or acid yields *1-carboxy-6-aminophenyl-3-arsinic acid* (*anthranilarsinic acid*),  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{AsO}(\text{OH})_2$ , crystallising in slender needles, m. p.  $245^\circ$  (decomp.). The latter substance may be diazotised and coupled with amines and phenol. An aqueous solution of the diazo-sulphate when heated yields *1-carboxy-6-hydroxyphenyl-3-arsinic acid* (*salicylarsinic acid*),

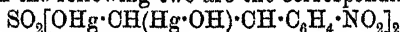


which crystallises in small, transparent, rhombic plates and commences to decompose at  $325^\circ$ .

*1-Carboxy-5-acetaminophenyl-2-arsinic acid*,  $\text{C}_9\text{H}_{10}\text{O}_5\text{NAs}$ , crystallises in brittle needles, m. p. about  $260^\circ$  (decomp.). It is decomposed by acids, but is hydrolysed by alkalis, yielding *1-carboxy-5-aminophenyl-2-arsinic acid*,  $\text{C}_7\text{H}_5\text{O}_3\text{NAs}$ , which forms thin, transparent, colourless leaflets.

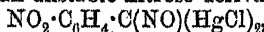
W. H. G.

**Preparation of *o*-Nitrobenzaldehyde and *o*-Nitrobenzaldoxime.** KALLE & Co. (D.R.-P. 199147. Compare Abstr., 1907, i, 1046).—The dimercury compound of *o*-nitrotoluene has the formula  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\langle\text{Hg}\rangle\text{O}$ , and yields two series of (basic and normal) salts, of which the following two are the corresponding *sulphates*:

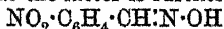


and  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\langle\text{Hg}\cdot\text{O}\rangle\text{SO}_2$ .

The sparingly soluble *dinitrite*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{Hg}\cdot\text{NO}_2)_2$ , is best prepared by shaking together a paste of the mercury base, sodium nitrite, and 10% sulphuric acid. When treated with 25% hydrochloric acid, this dinitrite decomposes, giving rise to *o*-nitrobenzaldehyde and *o*-nitrobenzaldoxime in approximately equal amounts. It is assumed that nitrous acid and an unstable nitroso-derivative,



are first formed, and that the latter is further decomposed into



and mercuric chloride; the nitrous acid reacts with some of the oxime, giving rise to the corresponding aldehyde.

G. T. M.

## Organic Chemistry.

**Density of Methane; Atomic Weight of Carbon.** GEORGES BAUME and F. LOUIS PERROT (*Compt. rend.*, 1909, 148, 39—42).—The methane was prepared by the action of water on magnesium methyl iodide, and, after being passed through different reagents and then dried, was purified by liquefaction and fractional distillation. The density determinations were carried out in three bulbs of different size in the usual way. As a mean of nine moderately concordant experiments, the weight of a litre of the gas at 0°/760 mm. is 0.7168 gram. From the results, the atomic weight of carbon is calculated by the physico-chemical methods of Leduc, D. Berthelot, and Guye respectively; the mean value is  $C=12.004$  ( $H=1.0077$ ), in good agreement with the accepted value. G. S.

**Hydrocarbons,  $C_5H_{12}$ ; New Synthesis of Tetramethylmethane [Dimethylpropane].** ENOS FERRARIO and F. FAGETTI (*Gazzetta*, 1908, 38, ii, 630—634).—Dimethylpropane may be prepared by the action of (1) methyl magnesium iodide on *tert.*-butyl iodide (15—20% yield); (2) *tert.*-butyl magnesium iodide on methyl iodide (15—20% yield); (3) methyl sulphate on *tert.*-butyl magnesium iodide (75% yield). The *tert.*-butyl alcohol required in the last of these syntheses may be obtained in 75% yield by the action of carbon dioxide on methyl magnesium iodide (compare Grignard, *Abstr.*, 1904, i, 213). T. H. P.

**Synthesis of Ethylene from Carbon Monoxide and Hydrogen by Contact with Nickel and Palladium.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1588—1590).—When a mixture of approximately equal volumes of carbon monoxide and hydrogen is passed over pieces of coke impregnated with reduced nickel and palladium and heated at 95—100°, no formaldehyde is produced, the gaseous mixture obtained consisting of carbon monoxide, hydrogen, and ethylene, with a small proportion of air. In one experiment, the gases contained 6.6% of ethylene, and in another, 8.3%. The first part of the reaction probably consists in the reduction of the carbon monoxide to water and the methylene group:  $CO + 2H_2 = H_2O + CH_2$ , two methylene groups then combining to form ethylene.

Attempts to absorb the ethylene in the mixture of gases formed by means of bromine or bromine water met with failure, which the author accounts for by the great dilution of the ethylene with other gases. A concentrated solution of potassium mercuric iodide,  $HgI_2 \cdot 2KI$ , in sodium hydroxide constitutes a far more certain absorbent of ethylene than either bromine or bromine water.

The formation of ethylene instead of methane, which would be expected from the results of Sabatier and Senderens and of Ipatieff, is not in accord with the thermal changes occurring during these

reactions, which would indicate the formation of methane rather than ethylene.

When a mixture of carbon dioxide and hydrogen is passed over coke impregnated with nickel and palladium and heated at 95—100°, the resultant gases do not contain either formaldehyde, ethylene, or methane.

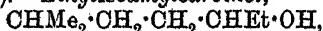
At higher temperatures, also, no formation of formaldehyde is observable, carbon dioxide and hydrogen yielding ethylene and methane; this observation is not in accord with those of other investigators, who state that only methane is formed by the reduction of carbon dioxide. The carbon dioxide first undergoes reduction in the presence of heated coke to carbon monoxide, which is then reduced to ethylene and methane.

T. H. P.

**Preparation of Nitromethane.** WILHELM STRINKOFF (*Ber.*, 1908, 41, 4457—4458).—A modification of the original Preibisch method (this Journ., 1874, 462), which not only gives a much better yield of nitromethane, but also avoids the evolution of hydrogen cyanide. A solution, containing potassium chloroacetate (=200 grams of acid) and 300 grams of potassium nitrite in one litre of water, is heated in a flask fitted to a condenser until carbon dioxide begins to be evolved. The reaction then proceeds, and the nitromethane distils in the steam. The yield is 49% of the theoretical.

W. R.

**Ethylisoamylcarbinol and Methylisohexylcarbinol.** ARMAND BUELENS (*Bull. Acad. roy. Belg.*, 1908, 921—929. Compare Henry, *Abstr.*, 1906, i, 723).—*Ethylisoamylcarbinol*,



m. p. 61°, b. p. 165—166°,  $D_4^{20}$  0.8084,  $n_D^{20}$  1.42011, obtained by the action of magnesium *isoamyl* bromide on propaldehyde, is a liquid of pleasant odour and burning taste. The *acetyl* derivative, b. p. 184—185°,  $D_4^{20}$  0.8554,  $n_D^{20}$  1.41602, is a colourless, mobile, pleasant-smelling liquid.

*Methylisohexylcarbinol*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OH}$ , b. p. 171—172°/760 mm.,  $D_4^{20}$  0.8128,  $n_D^{20}$  1.42381, obtained by the interaction of magnesium *isohexyl* bromide with acetaldehyde, is a liquid of agreeable odour and sharp taste. The *acetate*, b. p. 187—188°/768 mm.,  $D_4^{20}$  0.8494,  $n_D^{20}$  1.4137, is a colourless, mobile, pleasant-smelling liquid. *Methyl isohexyl ketone*, b. p. 166°/770 mm.,  $D_4^{20}$  0.8151, obtained by oxidising the alcohol with chromic acid, is a colourless liquid, and forms a sodium bisulphite compound. The *methyl ether*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{OMe}$ , b. p. 149—150°/760 mm.,  $D_4^{20}$  0.7945, obtained by the action of chloroethyl methyl ether,



on magnesium *isohexyl* bromide, is a liquid of agreeable odour.

*β-Methylheptane*,  $\text{CHMe}_2 \cdot [\text{CH}_2]_4 \cdot \text{CH}_3$ , b. p. 118°/760 mm.,  $D_4^{20}$  0.7134,  $n_D^{20}$  1.39807, was obtained by the action of metallic sodium on a mixture of propyl iodide and *isoamyl* iodide, the normal hexane and the decane simultaneously formed being eliminated by fractional distillation. It is a colourless, very mobile, pleasant-smelling liquid.

The *isohexyl* alcohol, b. p. 147—148°, used in the research was prepared by the action of trioxymethylene on magnesium *isoamyl* bromide in presence of zinc chloride. *isoHexyl bromide*, b. p. 146—147°/760 mm.,  $D^{20}_D$  1.1683,  $n_D$  1.44897, obtained by saturating the alcohol with hydrogen bromide and warming in a closed vessel, is a colourless, mobile liquid of slight, not unpleasant odour.

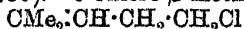
T. A. H.

**Direct Dehydration of Certain Tertiary Alcohols.** LOUIS HENRY (*Compt. rend.*, 1908, 147, 1260—1262).—In the production of  $\beta\gamma$ -dimethyl- $\Delta^a$ -butylene and  $\beta\gamma$ -dimethyl- $\Delta^s$ -butylene by heating dimethylisopropylcarbinol with acetic anhydride containing a small amount of sulphuric acid (Abstr., 1907, i, 374), it was originally considered that, since only a very small proportion of sulphuric acid was present, the acetic anhydride acted as the dehydrating agent. Delacre, however, has shown (Abstr., 1907, i, 459) that dimethylisopropylcarbinol is transformed into its acetate by the action of acetic anhydride. Thus the sulphuric acid must be the active agent in the reaction, which seems to be a curious instance of catalysis. That the acetic anhydride takes part in the reaction, however, is shown by the fact that it is only in the presence of a few drops of sulphuric acid that the decomposition of the acetate already formed takes place more easily and more rapidly than that of the alcohol as such.

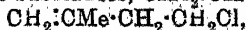
Contrary to the behaviour of dimethylisopropylcarbinol, *cyclopropylmethylcarbinol* (Abstr., 1908, i, 881), when heated with acetic anhydride containing a little sulphuric acid, does not undergo dehydration, but is completely transformed into its acetate. The conclusion is drawn that the existence of a closed chain in the molecule confers stability on the alcohol.

E. H.

**$\gamma\gamma$ -Dimethylallylcarbinol.** MAURICE VAN AERDE (*Bull. Acad. roy. Belg.*, 1908, 929—939).— $\epsilon$ -Chloro- $\beta$ -methyl- $\Delta^s$ -amylene,



(Henry, Abstr., 1907, i, 106), yields a liquid *dibromide*,  $D^{20}_D$  1.71, and is converted into the corresponding acetate (the *dibromide* of this has  $D^{20}_D$  1.551) by heating in closed tubes with potassium acetate and acetic acid, and this, on treatment with potassium carbonate, yields  $\gamma\gamma$ -dimethylallylcarbinol,  $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 157—158°/771 mm.,  $D^{20}_D$  0.8615,  $n_D$  1.44416, a colourless liquid with a slight terebinthinous odour and sharp, acrid taste. On re-conversion into the *acetate*,  $D^{20}_D$  0.9183,  $n_D$  1.4308, by the action of acetic anhydride, the product obtained boiled at 165—175°, which would seem to indicate that the alcohol and chloride referred to above are mixtures, in spite of their constant boiling points. Having regard to its method of formation, the supposed chloride might consist of the two substances,  $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$  and



but it does not yield acetone on oxidation with chromic acid, as the second suggested constituent should do.

On adding acetic anhydride to the mixture resulting from the

action of magnesium methyl bromide on ethyl  $\gamma$ -chlorobutyrate (Abstr., 1907, i, 106), adding water, and extracting with ether, a mixture of  $\epsilon$ -chloro- $\beta$ -methylpentane- $\beta$ -ol,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \text{Cl}$  (*loc. cit.*), and dimethyltetramethylene oxide,  $\text{O} \begin{array}{c} \text{CMe}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{array}$ , was obtained in place of the expected chloroacetin,  
 $\text{CH}_2 \text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{OAc}$ .

T. A. H.

**Physico-chemical Properties of Ethylene Glycol and of its Solutions in Water.** F. SCHWERS (*Bull. Acad. roy. Belg.*, 1908, 814—854).—The author has determined the densities of ethylene glycol and of its mixtures with water at temperatures from 0—100°, the specific heats of ethylene glycol and its mixtures with water, and the heats developed when it is mixed with water in various proportions. From the results obtained, which are given both in tabular and in graphic form, the following conclusions are drawn: (1) Ethylene glycol has  $D_4^0$  1.12570, and its expansion by heat can be represented by the expression:

$$V_t = V_0(1 + 0.0005657t + 0.0000017074t^2 + 0.00000000293t^3).$$

(2) A contraction in volume, accompanied by a development of heat, occurs when ethylene glycol is mixed with water in any proportion. At 0° the maximum contraction (1.545% of the initial volume) is observed with a concentration of 58% of glycol and 42% of water, corresponding with the hydrate,  $2\text{C}_2\text{H}_4(\text{OH})_2, 5\text{H}_2\text{O}$ . The contraction decreases generally with increase in temperature, but between 50° and 70° a slackening in the rate of this decrease is observed for all concentrations, and is indicated by a flattening of the curves between these temperatures. This phenomenon, which seems to be connected with the boiling points of the components of the mixture, is also exhibited by mixtures of glycerol and water between 70° and 90°. Mixtures of the monohydric alcohols with water of certain concentrations undergo the same contraction at all temperatures, but a similar behaviour is not observed with aqueous solutions of the diols and triols. (3) The specific heat of ethylene glycol is 0.563 at 20° and 0.591 at 35°, whilst that of its aqueous solutions is always greater than that calculated additively from the specific heats of the glycol and of water (=1). (4) The heat developed by mixing glycol with water reaches a maximum for the concentration of 37% of glycol and 63% of water, which corresponds with the hydrate,  $\text{C}_2\text{H}_4(\text{OH})_2, 6\text{H}_2\text{O}$ . It decreases with rise in temperature, but the diminution is relatively small, so that it is still positive at the boiling point. The system ethylene glycol—water follows the thermodynamic rule that the difference between the calculated and observed specific heats is equal to the coefficient of the heat of admixture.

In all the above respects, the properties of the diols are intermediate between those of the mono- and tri-hydric alcohols. E. H.

**Expansion of Ethyl Ether and of Some Mixtures of the Ether and Ethyl Alcohol.** WILLY BEIN (*Abhand. K. Normalgleichungskom.*, 1908, 7, reprint from author).—The density, at 5°, 10°, 15°, 20°, 25°, 30°, 35°, 40°, 45°, 50°, 55°, 60°, 65°, 70°, 75°, 80°, 85°, 90°, 95°, 100°, is given for pure ethyl ether and for mixtures with ethyl alcohol in the following table:

15°, 20°, and 25°, of the purest commercial ethyl ether (Kahlbaum),  $D_{4}^{15} = 0.7200$ , of a specimen of ordinary commercial ether,  $D_{4}^{15} = 0.7274$ , and of two mixtures obtained by mixing Kahlbaum's ether with 5% and 10% of a commercial spirit containing 90% of alcohol by volume, have been determined. The two latter specimens had  $D_{4}^{15} = 0.7280$  and  $0.7354$  respectively. As the investigations were carried out mainly for revenue purposes, no measurements were made with absolutely pure ethyl ether. The density determinations were made in a U-shaped dilatometer, the upper parts of the two branches being long, graduated capillary tubes; at the extreme ends the capillaries were so narrow that no appreciable error was caused by leaving them open.

The density results are probably accurate to some units in the fifth decimal place, and for convenience of reference they are also tabulated to 1 in 10,000. The mean expansion for 1°,  $\epsilon_t = [(V_t/V_0) - 1]t$ , between 0° and  $t^\circ$  is as follows, allowance being made for the expansion of the glass:

Purest ether.....	0.001522 + 0.0000040t.
Ether of D = 0.7280...	0.001480 + 0.0000042t.
„ D = 0.7354...	0.001438 + 0.0000040t.

The results are compared in detail with those obtained by previous observers.

In an appendix, the impurities which may be present in commercial ethyl ether, and the methods of detecting and removing them are given. G. S.

**Alkylated Halohydrin and Vinyl Ethers.** PAUL HÖRING (*Ber.*, 1908, 41, 4459—4460. Compare *Abstr.*, 1908, i, 497).—*Polemical.* A reply to Houben (*Abstr.*, 1908, i, 935). W. H. G.

**Action of Alkalis on Sodium Alkyl Thiosulphates.** T. SLATER PRICE and DOUGLAS F. TWISS (*Ber.*, 1908, 41, 4375—4378. Compare *Trans.*, 1908, 93, 1395).—The formation of disulphides by the action of alkalis on complex organic thiosulphates was observed originally by Berntsen (*Abstr.*, 1889, 775). The existence of Gutmann's thioethyl hydroperoxide (*Abstr.*, 1908, i, 497) is questioned. Fromm's experiments (*ibid.*, 969) are also regarded as pointing to the non-existence of this compound. The authors' previous view of the reaction between alkalis and alkyl thiosulphates is adhered to.

J. J. S.

**Indirect Analysis by means of the Dilatometer. Lower Hydrate of Sodium Acetate.** W. LASH MILLER (*J. Physical Chem.*, 1908, 12, 649—654).—When sodium acetate trihydrate is heated, it partly melts at 58°, with formation of a solution and separation of a new salt occurring in leaflets. The leaflets consist of a normal acetate of sodium, but they cannot readily be separated from the solution for purposes of analysis.

It is shown, however, on the basis of the phase rule, that the composition of the leaflets can be deduced by adding to a definite quantity

of the trihydrate a known amount of the anhydrous acetate, and determining the proportion of trihydrate present in equilibrium at 58°. The amount of trihydrate present has been determined by dilatometer measurements. In this way it is shown that the leaflets consist of the anhydrous salt, a conclusion confirmed by the direct experiments of Green (next abstract). G. S.

**The Melting Point of Hydrated Sodium Acetate. Solubility Curves.** W. F. GREEN (*J. Physical Chem.*, 1908, 12, 655—660).—The leaflets separating when sodium acetate is heated to its apparent melting point at 58° have been drained at 95°, and shown by analysis and m. p. determination to be the anhydrous salt.

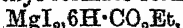
The solubility of the anhydrous salt has been determined from 0° to 123°, the boiling point of the saturated solution, and that of the trihydrate from its cryohydric point to 58°. The latter temperature is a transition point, at which the reaction  $\text{CH}_3\cdot\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O} = 0.092\text{CH}_3\cdot\text{CO}_2\text{Na} + \text{solution}$  ( $0.098\text{CH}_3\cdot\text{CO}_2\text{Na} + 3\text{H}_2\text{O}$ ) is in equilibrium.

The lowest temperature at which a clear solution can be obtained is 79°, when the solution saturated with the anhydride has the same composition as the crystals of the trihydrate. G. S.

**Molecular Compounds of Magnesium Bromide and Iodide with Derivatives of Acetic and other Organic Acids.** BOB N. MENSCHUTKIN (*Zeitsch. anorg. Chem.*, 1909, 61, 100—118. Compare Abstr., 1907, i, 19, 395).—Magnesium iodide combines with methyl acetate, forming the compound  $\text{MgI}_2\cdot 6\text{CH}_3\cdot\text{CO}_2\text{Me}$ . Mixture containing from 2.5% to 74.5% of the compound separate into two layers on melting. On the other hand, the ethyl, propyl, and butyl acetate compounds,  $\text{MgI}_2\cdot 6\text{CH}_3\cdot\text{CO}_2\text{Et}$ ,  $\text{MgI}_2\cdot 6\text{CH}_3\cdot\text{CO}_2\text{Pr}$ , also  $\text{MgI}_2\cdot 6\text{CH}_3\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$ , give regular freezing-point curves, and do not separate into two liquid layers. Separation into two layers is brought about in the case of the ethyl acetate compound by the addition of a little water.

Magnesium bromide forms compounds containing 3 mols. of ester which, however, crystallise badly.

Magnesium iodide and ethyl formate form a compound,



which is less hygroscopic than the acetate compounds.

The following compounds have been prepared, but not further described:

$\text{MgBr}_2\cdot 2\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Et}$ , m. p. about 110°;  $\text{MgBr}_2\cdot 2\text{C}_6\text{H}_5\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$ , m. p. about 130°;  $\text{MgI}_2\cdot 3\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Me}$ , m. p. 115—117°;  $\text{MgI}_2\cdot 3\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Et}$ , m. p. 105°.

Ethyl malonate gives  $\text{MgBr}_2\cdot 2\text{CH}_2(\text{CO}_2\text{Et})_2$ , m. p. 135°, and  $\text{MgI}_2\cdot 4\text{CH}_2(\text{CO}_2\text{Et})_2$ , m. p. about 115°. C. H. D.

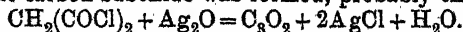
**The Waxes of the Coniferae. A New Group of Natural Principles.** J. BOUGAULT and LÉON BOURDIER (*Compt. rend.*, 1908, 147, 1311—1314).—By employing the method described by Bourquelot (*Pharm. Chim.*, 1901, [vi], 14, 481), the authors have isolated white,

crystalline powders, resembling certain known vegetable waxes in appearance, from many of the Coniferae, for example, from *Juniperus Sabina*, *J. communis*, *Picea excelsa*, *Pinus sylvestris*, and *Thuja occidentalis*. Kawaler, the only previous worker on these substances (*J. pr. Chem.*, 1853, 60, 321; 1855, 64, 16), owing to the defective method used, obtained erroneous results. The purified wax is not a simple substance, that from *J. Sabina* having m. p. 73—78° and yielding, on repeated recrystallisation, a series of substances having m. p.'s 65° to 84°. All the substances isolated, however, have the following properties: they are acids with an acidity value varying from 25 to 54 (indicating a molecular weight of 2000—1000 if they are monobasic acids), contain an alcohol group, and are esters with saponification values of about 230. All their saponification products are acids, that is, the waxes do not give any substances analogous to glycerol, or cetyl or melissyl alcohol. Thus the products of saponification are alcohol-acids, and from the results obtained on acetylation, seem to contain only a single alcohol and carboxyl group. So far only two of these acids have been isolated. The first has the composition,  $C_{16}H_{32}O_3$ , of a hydroxypalmitic acid, it has m. p. 95°, and is designated *juniperic acid*. The second, *sabinic acid*, m. p. 84°, seems to be a hydroxylauric acid,  $C_{12}H_{24}O_3$ . By connoting the results obtained, the authors deduce the scheme

$R \cdot CH(OH) \cdot [CH_2]_n \cdot CO \cdot O \cdot CHR' \cdot [CH_2]_m \cdot CO \cdot O \cdot CHR'' \cdot [CH_2]_p \cdot CO_2H$  for the constitution of the waxes,  $R$ ,  $R'$ ,  $R''$ , etc., and  $n$ ,  $m$ ,  $p$  being either identical or different. The frequent appearance of juniperic acid suggests that they are generally identical. The name *etholides* is proposed for this group of natural substances, which probably differ by the number of acid-alcohol molecules associated in them rather than by differences in the acid-alcohol molecules themselves. They thus resemble the polypeptides more nearly than the polysaccharides.

E. H.

**Ketens. XI. New Method of Formation of Carbon Suboxide.** HERMANN STAUDINGER and ST. BEREZA (*Ber.*, 1908, 41, 4461—4465. Compare Staudinger and Ott, *Abstr.*, 1908, i, 602).—In attempting to prepare malonic anhydride by acting on malonyl chloride in ether or ethyl acetate with silver, lead, or zinc oxide, it was found that carbon suboxide was formed, probably thus:



Carbon suboxide is also obtained when malonyl chloride is treated with either silver oxalate or malonate; however, in none of these cases does the yield of carbon suboxide exceed 10%.

Silver malonate interacts with acid chlorides, such as cinnamoyl chloride, yielding small quantities of carbon suboxide; the latter must result from the decomposition of malonic anhydride or a mixed anhydride; consequently, malonic anhydride differs from its alkyl derivatives in that it yields carbon suboxide and not keten when it decomposes. Acetyl chloride forms with silver malonate a substance which is probably identical with that obtained by Diels and Lalin (*Abstr.*, 1908, i, 939) by acting on carbon suboxide with acetic acid. It is also probable that the analogous compound derived from carbon

suboxide and formic acid (*loc. cit.*) is a mixed anhydride of formic and malonic acid having the formula  $\text{CH}_2(\text{CO}\cdot\text{O}\cdot\text{CHO})_2$ . A compound having this constitution, when heated, would decompose, yielding carbon monoxide, carbon suboxide, carbon dioxide, acetic acid, and formic acid.

A 50–80% yield of carbon suboxide may be readily obtained by treating a solution of dibromomalonyl chloride in ether or ethyl acetate with zinc shavings.

*Dibromomalonyl chloride*,  $\text{CBr}_2(\text{COCl})_2$ , prepared by the action of phosphorus pentachloride on an ethereal solution of dibromomalononic acid, is a colourless oil, b. p. 75–77°/15 mm., which solidifies to a colourless, crystalline mass at the ordinary temperature. It reacts with aniline, forming *dibromomalonanilide*,  $\text{CBr}_2(\text{CO}\cdot\text{NHPh})_2$ , compact crystals, m. p. 143–144°. W. H. G.

**Action of Zinc Dust at High Temperatures on Various Types of Aliphatic and Aromatic Acids.** ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1909, [iv], 5, 11–19).—A continuation of previous work (Abstr., 1901, i, 251; 1903, i, 396) on the products of the distillation of acids with zinc dust. The acids were mixed with from three to four times their weight of zinc dust, and heated at 350–400°.

Succinic acid yielded carbon dioxide and inflammable gases, composed principally of hydrogen, water, and liquid olefines. The residue in the flask contained some carbon and zinc carbonate. Oxalic acid gave hydrogen, carbon dioxide, carbon monoxide, and water. Benzoic acid furnished hydrogen, carbon dioxide, water, benzene, benzaldehyde, some unchanged benzoic acid, and a little naphthalene. The decomposition which ensued with cinnamic acid was very complicated. The gases evolved consisted of carbon dioxide, hydrogen, and some hydrocarbons. The liquid distillate included water, benzene, toluene, xylene, styrene, diphenyl, naphthalene and its homologues, stilbene, fluorene, fluoranthrene, homologues of anthracene and phenanthrene, toluene, and phenylmethanes (?) with some tarry matters. The residue in the flask contained carbon and some zinc carbonate. Distillation of cinnamic acid with lime showed that styrene is not, as is generally supposed, practically the sole product of the reaction. The distillate resembled in composition that described above, but contained more benzene and a little benzaldehyde.

Phthalic acid gave carbon dioxide, hydrogen, gaseous hydrocarbons, water, benzene, phthalic anhydride, and tar. T. A. H.

**Action of Sulphuric Acid on Acetaldehyde and Paracetaldehyde. Preparation of Crotonaldehyde.** MARCEL DELÉPINE (*Compt. rend.*, 1908, 147, 1316–1318\*).—The method of preparing crotonaldehyde described previously (Abstr., 1902, i, 133) has been improved by using paracetaldehyde instead of acetaldehyde. Paracetaldehyde (50 grams) is added in portions of 10–15 grams to ordinary concentrated sulphuric acid (250 c.c.) contained in a flask, which is continually shaken and cooled by a stream of cold water. After fifteen minutes, the product is diluted to 2 litres with water and

\* and *Ann. Chim. Phys.*, 1909, [viii], 16, 136–144.

distilled. By rectification of the product, 43% of the theoretical yield of crotonaldehyde is obtained. In the reaction there are also formed a compound,  $C_8H_{12}O_3$ , b. p. 92—98°/30 mm., which seems to be a bimolecular polymeride of crotonaldehyde, and a considerable amount of resin. The new polymeride differs from those described by Kekulé (*Annalen*, 1872, 162, 105), Raper (*Trans.*, 1907, 91, 1831), and Zeisel and Bitó (*Abstr.*, 1908, i, 761) in that it forms a *semicarbazone*,  $C_9H_{15}O_2N_3$ , m. p. 191—194°, and a stable *oxime*, m. p. 106°. The resins formed are fawn-coloured, and on oxidation with nitric acid give oxalic acid and a yellow, amorphous substance, which dissolves in ammonia to an orange solution. E. H.

**Anodic Oxidation of Aldehydes.** GEORGE W. HEIMROD and PHOEBUS A. LEVENE (*Ber.*, 1908, 41, 4443—4448).—It has already been shown that acetaldehyde is a good depolariser in acid solution (Dony-Hénault, *Abstr.*, 1900, ii, 644) and in alkali solution (Baur, *Abstr.*, 1902, i, 77), and further, Law (*Trans.*, 1905, 87, 198) obtained quantities of carbon dioxide and monoxide as well as the corresponding fatty acid on electrolytic oxidation.

Acetaldehyde in sodium sulphate or 0.85*N*-sulphuric acid solution at 4—5° with a current of 1 ampere, using a spiral platinum electrode, is oxidised almost quantitatively to acetic acid, only small quantities of the oxides of carbon being liberated. In 0.9*N*-sodium hydroxide solution, however, only 92% of the oxygen is absorbed by the aldehyde, a large amount of carbon monoxide, dioxide, and oxygen being liberated in the anode gas. Formic acid is found in the liquid, and it is probable that acetic acid is only formed in small amount.

Butaldehyde and isobutaldehyde in *N*-alkali solution give only small amounts of acid and a large volume of carbon dioxide; in the latter case, acetone was found, but formic acid could not be detected.

W. R.

**Syntheses by means of Mixed Organo-metallic Zinc Derivatives,  $\beta$ -Ketone Alcohols, and  $\alpha\beta$ -Acyclic Unsaturated Ketones.** EDMOND E. BLAISE and M. MAIRE (*Ann. Chim. Phys.*, 1908, [viii], 15, 556—576).—Mainly a résumé of work already published (compare *Abstr.*, 1907, i, 749; 1908, i, 79, 248, 318, 596); the following compounds are described for the first time:  $\gamma$ -Hydroxy- $\gamma$ -ethylhexan- $\delta$ -one,  $OH \cdot CEt_2 \cdot COEt$ , b. p. 68°/11 mm., prepared by the action of magnesium ethyl iodide on ethyl semi-ortho-oxalate;  $\gamma$ -methyl- $\Delta^7$ -hepten- $\epsilon$ -one,  $OMeEt \cdot CH \cdot COEt$ , b. p. 164°, forms a *semicarbazone*, m. p. 159°; ethyl acetoxy-sec.-butyl ketone [ $\alpha$ -acetoxy- $\beta$ -ethylpentan- $\gamma$ -one],  $OAc \cdot CH_2 \cdot CHEt \cdot COEt$ , b. p. 102°/12 mm.;  $\gamma$ -methylenehexan- $\delta$ -one,  $CH_2 \cdot CEt \cdot COEt$ , b. p. 137°;  $\beta$ -acetoxy- $\gamma$ -ethylhexan- $\delta$ -one,  $OAc \cdot CHMe \cdot CHEt \cdot COEt$ , b. p. 102°/12 mm.;  $\beta$ -methyl- $\Delta^6$ -hexen- $\delta$ -one,  $OMe \cdot CH \cdot COEt$ , b. p. 148°, forms a *semicarbazone*, m. p. 162°. Ethyl  $\beta$ -hydroxy- $\alpha$ -ethylisovalerate,  $OH \cdot CMe_2 \cdot CEt \cdot CO_2Et$ , b. p. 84°/9 mm.; the corresponding acid has m. p. 73°; ethyl  $\beta\beta$ -dimethyl- $\alpha$ -ethylacrylate,  $CMe_2 \cdot CEt \cdot CO_2Et$ , b. p. 167°, obtained from the above ester by the action of phosphoric acid; the corresponding acid has

b. p. 100°/10 mm., and the *chloride*, b. p. 49°/13 mm., reacts with zinc ethyl to form  $\beta$ -methyl- $\gamma$ -ethyl- $\Delta^8$ -hexen- $\delta$ -one,  $\text{CMe}_2\cdot\text{CEt}\cdot\text{COEt}$ , b. p. 164°, of which the *semicarbazone* has m. p. 117°. M. A. W.

**Formation of Hydrocelluloses by means of Sulphuric Acid.** GEORG BÜTTNER and J. NEUMAN (*Zeitsch. angew. Chem.*, 1908, 21, 2609—2611. Compare Girard, *Abstr.*, 1879, 779; Bumke and Wolfenstein, *Abstr.*, 1899, 852; Tauss, *Ding. Poly. J.*, 1889, 286).—Amyloid, prepared by leaving cotton wool in contact with sulphuric acid (1.53) for several days, then carefully precipitating and washing, has the composition C 41.89, 42.00, and H 6.0, 6.07%.

An ideal hydrocellulose can be obtained by Ulzer's method (Wagner's *Jahresber.*, 1905, 192). The cotton is impregnated with 4% sulphuric acid, pressed, and kept at the ordinary temperature for four days or until dry, and then carefully heated at 75° for eight hours. When touched, the mass falls to a white powder, and its suspensions in acid have a colloidal nature and do not clear when kept. Analyses of the washed material dried at 100° gave C 43.86, H 5.41%, which agree with values required for the formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n\cdot\text{H}_2\text{O}$ .

When this hydrocellulose is further treated with 50% sulphuric acid, sometimes it does not undergo any further change, sometimes it yields compounds of the types  $3\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{H}_2\text{O}$  and  $2\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{H}_2\text{O}$ .

The hydrocelluloses are white powders with a gritty feel, and are resistant to acids and alkalis. With sulphuric acid and acetic anhydride, they yield cellulose acetates, which can be precipitated by water. They are coloured blue by zinc chloriodide, or a solution of iodine in potassium iodide solution, and have reducing properties, but are not turned black by the oxidising action of the atmosphere (compare Girard). J. J. S.

**Humic Substances in Peat Wool ("Ouate de Tourbe").** L. ROGER and E. VULQUIN (*Compt. rend.*, 1908, 147, 1404—1406).—The humic acids extracted from peat wool by sodium hydroxide are derived from cellulose-like substances, from which they differ in containing more carbon and nitrogen. They contain neither pentosans nor hexosans; alcoholic hydroxyls still seem to be present, for acetyl derivatives and thiocarbonates can be formed, as in the case of cellulose. The benzene nucleus, the grouping  $\cdot\text{CH}_2\cdot\text{CO}$ , and double linkings are also present. G. B.

**Example of Isodimorphism. [Ethylamine Halides.]** H. MARAIS (*Compt. rend.*, 1909, 148, 45—47).—Ethylamine hydrochloride and the corresponding hydrobromide are monoclinic at the ordinary temperature. At 80°, the hydrochloride changes to a uniaxial modification, which fuses at 108°. At 83°, the hydrobromide is also changed to a uniaxial form, which melts at 146°. Further, in the superfused hydrobromide, an unstable, uniaxial form appears, which fuses at 118°, but under ordinary conditions rapidly changes to the stable form.

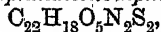
The monoclinic forms of the two compounds are miscible in all proportions, the temperature of transformation remains between 80°

and 83°. The forms obtained at higher temperatures are isomorphous, the stable form of one being isomorphous with the unstable form of the other. Further, as the composition approaches the point corresponding with 45% of the hydrobromide at 100°, the unstable forms tend to become relatively stable. G. S.

**Valyl-leucine Anhydride.** E. KRAUSE (*Monatsh.*, 1908, 29, 1119—1130).—The paper is mainly an account of unsuccessful experiments and of compounds already described (Fischer, Abstr., 1907, i, 684). *Valyl-leucine anhydride*, m. p. 273—274°, is formed by heating equal molecular quantities of valine and leucine esters at 180—190°, or equal quantities of valine and leucine in an evacuated tube at 340°. G. S.

**Some Amides of Amino-acids.** ERNST KOENIGS and BRUNO MYLO (*Ber.*, 1908, 41, 4427—4443).—The amides of amino-monocarboxylic acids are not easily obtained in the pure state, but it is found that the ethyl esters are converted into the amides by liquid ammonia, and, as a rule, they are unstable in the presence of water.

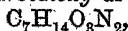
When the ester of glycine is treated with three times its volume of liquid ammonia, there is formed diketopiperazine, *glycylglycinamide*, and *glycinamide*,  $C_2H_6ON_2$ ; the latter compound crystallises from chloroform in needles, m. p. 65—67° (corr.). It is strongly alkaline and hygroscopic. The *dinaphthalenesulphonylglycinamide*,



from naphthalenesulphonyl chloride and amide, crystallises in slender needles, m. p. 201° (corr., decomp.);  $\beta$ -naphthalenesulphonamide is obtained on its hydrolysis with *N*/10-sodium hydroxide, showing that the two naphthalenesulphonyl radicles are attached to the amido-nitrogen and not to the amino-group. Carbethoxyglycinamide (Fischer, Abstr., 1903, i, 609) may also be prepared from the amide by the action of ethyl chlorocarbonate in the presence of alkali, and a 10% yield of hydantoin is obtained from carbethoxyglycinamide by the action of *N*/2-sodium hydroxide during twenty-four hours at the ordinary temperature.

*d-Alaninamide*,  $C_3H_8ON_2$ , crystallises from chloroform in colourless, slender prisms, m. p. 72° (corr.),  $[\alpha]_D + 6^\circ$  in 5.2% aqueous solution. The *dl*-alaninamide, prepared by liquid ammonia, agrees in all respects with that obtained by Franchimont and Friedmann in 1906. Carbethoxy-*dl*-alaninamide can be obtained in 86% yield from the amide (compare Fischer and Axhausen, Abstr., 1905, i, 689), and  $\alpha$ -methylhydantoin from the carbethoxy-compound has m. p. 146.5° (corr.).  $\beta$ -Naphthalenesulphonyl-*dl*-alaninamide,  $C_{18}H_{14}O_5N_2S_2$ , has m. p. 220° (corr., decomp.).

*dl*- $\alpha$ -Amino-*n*-butyramide,  $C_4H_{10}ON_2$ , crystallises in prisms, m. p. 74—75° (corr.), and yields carbethoxy-*dl*- $\alpha$ -amino-*n*-butyramide,



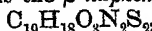
which forms colourless needles, m. p. 115—116° (corr.).  $\alpha$ -Ethyl hydantoin,  $C_5H_8O_3N_2$ , crystallises from chloroform in slender needles, m. p. 118—120° (corr.), and  $\beta$ -naphthalenesulphonyl-*dl*-aminobutyramide,  $C_{14}H_{16}O_5N_2S_2$ , has m. p. 251° (corr., decomp.).

*dl*-Valinamide,  $C_5H_{12}ON_2$ , only results after the ester and liquid

ammonia have been in contact three months; it has m. p. 78—80° (corr.), and yields  $\beta$ -naphthalenesulphonyl-dl-valinamide,  $C_{15}H_{18}O_3N_2S$ , of m. p. 256—257° (corr.); carbethoxy-dl-valinamide,  $C_8H_{16}O_3N_2$ , slender needles, m. p. 143—144° (corr.).

dl-Leucinamide,  $C_6H_{14}ON_2$ , has m. p. 106—107° (corr.); the  $\beta$ -naphthalenesulphonyl derivative has m. p. 176—178° (corr.); carbethoxy-dl-leucinamide,  $C_9H_{18}O_3N_2$ , m. p. 108°, and  $\beta$ -isobutylhydantoin (compare Pinner and Lifschütz, Abstr., 1887, 1055) is readily obtained from the preceding compound by shaking with sodium hydroxide.

dl-Phenylalaninamide,  $C_9H_{12}ON_2$ , crystallises in prisms, m. p. 138—140° (corr.), and yields the  $\beta$ -naphthalenesulphonyl compound,



of m. p. 164—166° (corr.), and the carbethoxy-dl-phenylalaninamide,  $C_{19}H_{16}O_3N_2$ , m. p. 141° (corr.).

l-Tyrosinamide,  $C_9H_{12}O_2N_2$ , crystallises from alcohol in large, flat prisms, m. p. 153—154°,  $[\alpha]_D^{20} + 19.49^\circ$  in water, and its decarboxy-derivative,  $C_{15}H_{20}O_6N_2$ , forms needles, m. p. 185° (corr.); the mono-carbethoxy-l-tyrosinamide,  $OH \cdot C_6H_4 \cdot CH_2 \cdot CH(NH \cdot CO_2Et) \cdot CO \cdot NH_2$ , has m. p. 155—157° (corr.). The  $\beta$ -naphthalenesulphonyl compound,  $C_{29}H_{24}O_6N_2S_2$ , has m. p. 204° (corr.).

Carbethoxy-l-asparagine,  $C_7H_{12}O_5N_2$ , crystallises from water, and has m. p. 169—171° (corr.); the  $\beta$ -naphthalenesulphonyl-l-asparagine,  $C_{14}H_{14}O_5N_2S$ , has m. p. 192—193° (corr.). W. R.

**Preparation of Glycocyamines or Guanino-acids.** HENRIK RAMSAY (*Ber.*, 1908, 41, 4385—4393. Compare Strecker, *Compt. rend.*, 1861, 52, 1212; Du villier, Abstr., 1880, 897; 1887, 850; Nencki and Sieber, Abstr., 1879, 70).—One of the simplest methods for the preparation of guanino-derivatives of fatty acids (glycocyamines) is warming the halogenated fatty acid with a large excess of guanidine (5—10 mols.) and a little water. With the simpler compounds up to bromoisohexoic acid, a temperature of 60° for a few hours is sufficient. With the derivatives of higher fatty acids, for example, bromopalmitic acid or  $\alpha$ -bromophenylacetic acid, eight hours at 100° or ten hours at 80° are necessary. Guaninoacetic,  $\alpha$ -guaninopropionic,  $\alpha$ -guanino-*n*-butyric,  $\alpha$ -guaninoisovaleric,  $\alpha$ -guaninoisohexoic,  $\alpha$ -guaninopalmitic, and  $\alpha$ -guaninophenylacetic acids have been prepared by this method.

$\alpha$ -Guaninopropionic acid (alacreatine) has m. p. 226° (corr.) when quickly heated, whereas Baumann gives (Abstr., 1873, 1024) m. p. 180°; the *nitrate* decomposes at 150°, and the *sulphate* at 155—160°.

$\alpha$ -Guanino-*n*-butyric acid (oxybutyrocyamine) crystallises from hot water in slender needles or rectangular prisms, and has m. p. 243—245° (corr., decomp.). The *nitrate* decomposes at 162°, and the *sulphate* at 165—168°.

$\alpha$ -Guaninoisovaleric acid (oxyvalerocyamine) forms rectangular plates, and has m. p. 242° (corr., decomp.). The *nitrate* decomposes at 172—176°, and the *sulphate* at 178—180°.

$\alpha$ -Guaninoisohexoic acid ( $\alpha$ -aminohexocyamine) crystallises in needles, and decomposes at 242—243° (corr.). The *nitrate* decomposes at 177—180°, and the *sulphate* at 182—185°.

*α-Guaninopalmitic acid*,  $\text{CH}_3 \cdot [\text{CH}_2]_{13} \cdot \text{C}(\text{CH}_2\text{N}_3) \cdot \text{CO}_2\text{H}$ , crystallises from methyl alcohol in octahedra, has m. p.  $173^\circ$  (corr., decomp.), and dissolves in alkalis and in concentrated acids. The *nitrate*,

$(\text{C}_{17}\text{H}_{35}\text{O}_2\text{N}_3)_2\text{HNO}_3$ , crystallises in slender, glistening needles, and has m. p.  $155-156^\circ$  (corr., decomp.). The *hydrochloride* decomposes at  $132-134^\circ$  (corr.).

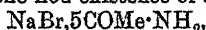
Phenylguaninoacetic acid (glycolylphenylguanidine),  $\text{CH}_4\text{N}_3 \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$ , appears to be identical with the product obtained by Berger (Abstr., 1880, 802) from phenyleyanamide and glycine. The *nitrate*,  $(\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3)_2\text{HNO}_3$ , decomposes at  $220-226^\circ$ , and the *hydrochloride* at  $255-258^\circ$  (corr.).  
J. J. S.

**Acetamide as a Solvent.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1415-1434).—The author has determined the solubility curves of various salts in acetamide, only salts being chosen for which the solubility curves in water have been worked out. The results show that acetamide closely resembles water, both in the form of the solubility curves of salts in it and in other properties, for example, the ionising power. It may, indeed, be expected that every salt which forms hydrates will give corresponding compounds with amides, those formed with formamide and acetamide approximating in their properties most closely to those formed with water.

No hydrate of potassium iodide is known, yet Walker and Johnson (Trans., 1905, 87, 1597) state that this salt forms with acetamide a stable compound,  $\text{KI} \cdot 6\text{COMe} \cdot \text{NH}_2$ , m. p.  $54^\circ$ . Besides the fact that compounds of such a type are usually formed by haloid salts of metals of the second and higher groups, the low m. p. given argues against the existence of this compound. The author's investigation of the system acetamide-potassium iodide characterises this system as one in which the components do not combine. The curve, which has a form very closely resembling that of the water-potassium iodide curve, consists of two branches: (1) the curve of lowering of the m. p. of acetamide by the addition of potassium iodide, and (2) the curve of solubility of the iodide in acetamide. These two branches meet in a eutectic point, about  $53^\circ$ , the composition there corresponding approximately with the formula  $\text{KI} \cdot 7 \cdot 1\text{COMe} \cdot \text{NH}_2$ . Crystallisation from methyl alcohol of mixtures of potassium iodide and acetamide of the compositions  $\text{KI} \cdot 6\text{COMe} \cdot \text{NH}_2$  to  $\text{KI} \cdot 7\text{COMe} \cdot \text{NH}_2$  yielded apparently homogeneous crystals, which, however, the microscope showed were merely mixtures of crystals of potassium iodide and acetamide. Hence the conclusion is drawn that Walker and Johnson's compound,  $\text{KI} \cdot 6\text{COMe} \cdot \text{NH}_2$ , does not exist.

The diagram for the system acetamide-sodium bromide indicates the existence of the compound,  $\text{NaBr} \cdot 2\text{COMe} \cdot \text{NH}_2$ , which decomposes at  $135-136^\circ$  (compare Titherley, Trans., 1901, 79, 413). Comparison of this diagram with that for the system water-sodium bromide shows that the three branches: (1) curve of lowering of m. p. of acetamide or water by addition of sodium bromide, (2) curve of solubility of

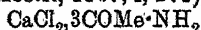
NaBr, 2H<sub>2</sub>O or NaBr, 2COMe·NH<sub>2</sub>, and (3) curve of solubility of pure sodium bromide, are practically identical in form in the two cases. The diacetamide compound is less stable than the dihydrate, a fact which may account for the non-existence of a compound,



corresponding with the pentahydrate.

The curve representing the lowering of the m. p. of acetamide by sodium iodide ends in a eutectic point, 41.5°, corresponding with NaI, 5COMe·NH<sub>2</sub>, from which starts the curve of solubility in acetamide of the compound, NaI, 2COMe·NH<sub>2</sub>, which decomposes at 125° (compare Titherley, *Trans.*, 1901, 79, 413). In this case, also, no acetamide compound is formed corresponding with the pentahydrate.

In the system acetamide-calcium chloride, the eutectic point is very low, namely, 46°, corresponding with CaCl<sub>2</sub>, 3COMe·NH<sub>2</sub>. Beyond this point comes the solubility curve of CaCl<sub>2</sub>, 6COMe·NH<sub>2</sub>, continuing to the m. p., 64°; this compound crystallises from methyl alcohol in hygroscopic plates. At 64° begins the solubility curve of the compound, CaCl<sub>2</sub>, 3COMe·NH<sub>2</sub>, which crystallises in hygroscopic needles decomposing at 186°, the solid phase beyond this temperature being probably CaCl<sub>2</sub>, COMe·NH<sub>2</sub>. Comparison of this diagram with that for the system water-calcium chloride shows that the solubility curves for CaCl<sub>2</sub>, 6COMe·NH<sub>2</sub> and CaCl<sub>2</sub>, 6H<sub>2</sub>O are very similar; with acetamide, however, no compounds are formed analogous to the α- and β-tetrahydrates and the dihydrate. Like the solubility curve of CaCl<sub>2</sub>, 3MeOH (compare *Abstr.*, 1907, i, 271), that of



also closely resembles that of CaCl<sub>2</sub>, 2H<sub>2</sub>O. The triacetamide compound decomposes the triacoholate with evolution of methyl alcohol, the compounds CaCl<sub>2</sub>, 3MeOH, CaCl<sub>2</sub>, 3COMe·NH<sub>2</sub>, and CaCl<sub>2</sub>, 2H<sub>2</sub>O being in order of increasing stability.

T. H. P.

**The Action of Chlorine on Carbamide, whereby a Dichlorocarbamide is Produced.** FREDERICK D. CHATTAWAY (*Proc. Roy. Soc.*, 1908, A, 81, 381—388).—*Dichlorocarbamide*, CO(NHCl)<sub>2</sub>, prepared by passing a very rapid stream of chlorine into a well-cooled solution of carbamide (20 grams) in water (40 c.c.), separates in thin, colourless plates. The compound is endothermic, and detonates when heated rapidly, owing to the formation of nitrogen chloride; when heated cautiously it has m. p. about 83° (decomp.). It is readily hydrolysed by water, and when kept in aqueous solution at the ordinary temperature, carbon dioxide, nitrogen, nitrogen chloride, and ammonium chloride are formed slowly. Acids and alkalis accelerate the hydrolysis, and also alter the nature of the end products; thus in presence of dilute acids all the chlorine in the compound is liberated as nitrogen chloride, but this compound is not formed when hydrolysis takes place in alkaline solution. The addition of potassium hydroxide causes violent evolution of nitrogen, the reaction taking place quantitatively in accordance with the following equation:



When carbamide is treated with excess of an alkaline hypobromite,

it is probable that a dibromocarbamide is first formed; the manner in which this undergoes hydrolysis is supposed by the author to furnish an explanation of the variable amount of nitrogen liberated during the decomposition.

Dichlorocarbamide is an acidic substance, and its aqueous solution reddens and then bleaches litmus; it shows all the reactions of a typical nitrogen chloride.

W. O. W.

**Desmotropy and Merotropy. V. Constitution of Hydrogen Cyanide.** ARTHUR MICHAEL and HAROLD HIBBERT (*Annalen*, 1909, 364, 64—76).—In continuation of previous work on the use of tertiary amines for distinguishing between enolic and ketonic derivatives (Michael and Smith, *Abstr.*, 1908, i, 943), the authors have applied this method towards the elucidation of the constitution of hydrogen cyanide.

When tertiary amines are brought into contact with anhydrous hydrogen cyanide at  $0^{\circ}$ , no salt is formed, but only a very slight polymerisation takes place. The rapidity of the latter decreases according to the series, triethyl-, tripropyl-, and triisooamyl-amine, that is, the capacity possessed by tertiary amines of polymerising hydrogen cyanide changes in the same relation as their capacity of enolising desmotropic ketones.

On the other hand, primary and secondary amines unite with hydrogen cyanide, forming unstable salts, and polymerisation does not take place. This can only be explained by the assumption that hydrogen cyanide exhibits keto-merotropy, and that primary and secondary amines can bring about merotropy in the substance, whilst tertiary amines can not. The authors' experiments show that the dialkyl- are less dissociable than the trialkyl-ammonium cyanides, that is, by substituting a hydrogen atom in  $\text{NH}_2\text{R}_2\text{NC}$  by a third alkyl radicle, the affinity between hydrogen and nitrogen is lessened, and hence secondary amines can effect merotropy in hydrogen cyanide with the formation of salts, whilst tertiary amines can not. The existence of trialkylammonium cyanide shows that if hydrogen cyanide were in the acidic form ( $\text{HNC}$ ), salt formation with tertiary bases would be possible. The conclusion is drawn, therefore, that hydrogen cyanide possesses the nitrile constitution  $\text{HCN}$ .

*Dipropyl- and diisobutyl-ammonium cyanides* are white, unstable salts; the latter has m. p.  $25^{\circ}$ . *Diisooamylammonium cyanide* is a white, crystalline, very unstable substance, m. p.  $68-70^{\circ}$ . *Piperidonium cyanide* is a white, crystalline salt, m. p.  $47-48^{\circ}$ ; it is more stable than the other cyanides examined, being decomposed only after twenty minutes on keeping in a desiccator under diminished pressure.

*isoButyl- and isooamyl-ammonium cyanides* remain, on evaporation of their solutions in a vacuum, partly as oils and partly crystalline. *Allylammonium cyanide* is a viscid, yellow oil. Aniline does not react with hydrogen cyanide. From the rise of temperature ( $15^{\circ}$ ) observed on mixing 90% aqueous hydrocyanic acid and triethylamine at  $0^{\circ}$ , the authors conclude that salt formation takes place. By treating the trialkylammonium chlorides with silver cyanide in methyl-alcoholic solution, double salts are obtained. Thus trimethylammonium chloride

gives the *salt*,  $\text{NMe}_3\text{HNC}\cdot\text{AgNC}$ , a white, crystalline substance, and triethylammonium chloride yields the *salt*,  $\text{NEt}_3\text{HNC}\cdot\text{AgNC}$ , in white, felted needles. On adding hydrogen cyanide to an equimolecular mixture of triethylamine and water, and evaporation of the solution in a vacuum, an oil was obtained which gave the above double salt with silver cyanide, and hence contained *triethylammonium cyanide*. Tripropylamine behaves similarly.

Dry ammonia combines instantly with dry hydrogen cyanide or its ethereal solution to form ammonium cyanide. J. C. C.

**Reaction between Ferric Salts and Thiocyanates.** ARNALDO BRIONI (*Gazzetta*, 1908, 38, ii, 638—640).—The author criticises Bongiovanni's views (*Abstr.*, 1908, i, 770, 859) on the interaction of a ferric salt and a thiocyanate. T. H. P.

**Simple Preparation of Mercuric Oxycyanide Solution from its Components.** ERWIN RUPP and F. LEHMANN (*Chem. Zentr.*, 1908, ii, 1816; from *Apoth. Zeit.*, 1908, 23, 793—794. Compare *Abstr.*, 1908, i, 770).—The reaction indicated by the equation  $\text{HgCl}_2 + \text{HgCy}_2 + 2\text{KOH} = \text{HgCy}_2\cdot\text{HgO} + 2\text{KCl} + \text{H}_2\text{O}$  is brought about by mixing aqueous solutions of molecular proportions of the components. For the preparation of a 1% solution, the following details are given: mercuric chloride, 5.8 grams, mercuric cyanide, 5.4 grams, dissolved in 800 grams of water, are added slowly to potassium or sodium hydroxide, 44.8 grams and water, 1000 grams. This solution contains 0.25% sodium chloride, or 0.32% potassium chloride. After keeping a solution of mercuric oxycyanide prepared in this manner for three months, the mercury, mercuric cyanide, and also the  $\text{HgCy}_2\cdot\text{HgO}$  component were estimated, and the results were in good agreement with  $\text{HgCy}_2\cdot\text{HgO}$ . J. V. E.

**Decomposition of Calcium Cyanamide.** FELIX LÖHNIS and R. MOLL (*Centr. Bakt. Par.*, 1908, ii, 22, 254—281. Compare *Abstr.*, 1908, ii, 220, and Kappen, *ibid.*, 414).—It is considered probable that, in dissolving, calcium cyanamide is converted into the compound  $\text{Ca}(\text{NH}\cdot\text{CN})_2$ , which subsequently decomposes into calcium hydroxide and cyanamide. The latter, when heated with lime, or when subjected to the action of carbon dioxide, yields first ammonium cyanate and then carbamide, which is converted by bacteria into ammonium carbonate.

A direct action of bacteria on cyanamide seems to be impossible. The bacteria flora found in solutions of the substance consists of varieties which are able to resist the poisonous actions of cyanamide and cyanates.

Dicyanodiamide is not attacked by bacteria, and there is no evidence that it exists in soils. N. H. J. M.

**Chemical Changes of Calcium Cyanamide in Manuring.** HUBERT KAPPEN (*Centr. Bakt. Par.*, 1908, ii, 22, 281—298. Compare *Abstr.*, 1908, ii, 728).—A criticism of Löhnis' results and conclusions. When calcium cyanamide is digested for some time with distilled

water at 60°, the filtered solution yields crystals of dicyanodiamide. The same change takes place at the ordinary temperature when solutions are kept for a long time. In the case of concentrated solutions, the sparingly soluble compound,  $\text{CN}\cdot\text{N}(\text{Ca}\cdot\text{OH})_2\cdot 6\text{H}_2\text{O}$ , and cyanamide are formed, the latter changing gradually into dicyanodiamide under the influence of alkali. In dilute solutions the calcium compound is not formed; calcium hydroxide separates in crystals, whilst the cyanamide all remains in solution and gradually polymerises.

N. H. J. M.

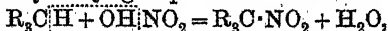
[Organo-mercury Compounds.] WALTER SCHRAUTH and WALTER SCHOELLER (*Ber.*, 1908, 41, 4479—4480. Compare *Abstr.*, 1908, i, 617).—A reply to Biilmann (this vol., i, 17). W. H. G.

Action of Nitric Acid on Saturated Hydrocarbons. II. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1570—1579. Compare *Abstr.*, 1908, i, 329).—Experiments on the action of nitric acid (D 1·2) on cyclohexane show that the yield of nitro-products diminishes, and that of acid oxidation products increases, as the proportion of nitric acid used increases.

Nitrocyclohexane,  $\text{C}_6\text{H}_{11}\cdot\text{NO}_2$ , is a colourless liquid with a characteristic smell, b. p. 109·5°/40 mm., 202°/742 mm. (decomp.),  $D_4^{20}$  1·0853,  $D_4^{25}$  1·0680,  $n_D^{20}$  1·4612.

This nitro-derivative is not an intermediate product in the oxidation of cyclohexane to adipic acid, as the latter is formed more readily from cyclohexane than from nitrocyclohexane. Such intermediate product is almost certainly unstable isonitrocyclohexane, which, immediately it is formed, is transformed partly into the stable nitrocyclohexane and partly into aldehyde (or ketone, according to the nature of the hydrocarbon), which undergoes further oxidation to the corresponding carboxylic acid.

The process of formation of tertiary nitro-derivatives is essentially different from that of primary or secondary nitro-compounds, the most striking difference lying in the mechanism of the formation of water in the two cases. In the first, water is formed from the tertiary hydrogen and the hydroxyl group of the nitric acid:



whilst with primary or secondary hydrocarbons, the oxygen atom only is taken from the nitric acid and the two hydrogen atoms from the hydrocarbon,  $\text{R}_2\text{C}\cdot\text{H}_2 + \text{O}\cdot\text{NO}\cdot\text{OH} = \text{R}_2\text{C}\cdot\text{NO}_2\text{H} + \text{H}_2\text{O}$ . T. H. P.

Preparation of 2-Chloro-3-nitrotoluene. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1908, 27, 455—457).—This paper contains details for the preparation of 2-chloro-3-nitrotoluene from 3-nitro-*o*-toluidine by means of the Sandmeyer reaction. An 84% yield is obtained, and the product has m. p. 21·5° (compare Wynne and Greeves, *Proc.*, 1905, 21, 151). W. O. W.

Bromination of Toluene. II. ARNOLD F. HOLLEMAN and J. J. POLAK with VAN DER LAAN and EUWES (*Rec. trav. chim.*, 1908, 27, 435—454. Compare *Abstr.*, 1906, i, 154).—The authors continue

the studies on the bromination of toluene, and in the present communication discuss the influence of temperature and dilution, and the action of catalysts on the ratio bromotoluenes : benzyl bromide.

Tables are given showing the percentages of benzyl bromide formed with various proportions of bromine and toluene at 25° and 50°. The authors claim that their results are more accurate than those obtained by Bruner and Dluska (Abstr., 1908, i, 146). On plotting in the form of a curve the values obtained by these authors in their experiments on the influence of temperature and comparing these with the data obtained by van der Laan, certain discrepancies appear, for which, at present, no explanation can be found.

To explain the action of catalysts, it has been supposed that these are capable of converting benzyl bromide into a mixture of bromotoluenes, no experimental evidence in support of this view could be obtained, however, since it was found that when benzyl bromide or chloride is boiled with toluene and ferric bromide, the sole product is *p*-benzyltoluene. A similar experiment, in which antimony tribromide was the catalyst, resulted in the formation of a small quantity of a liquid containing 50.9% bromine (bromotoluene requires 46.78%). Bromine itself was found to be incapable of behaving as an autocatalyst.

Cohen, Dawson, and Crosland (Trans., 1905, 87, 1034) have recorded the production of chlorotoluene by the action of nascent chlorine, generated by electrolysis, on boiling toluene. The hypothesis put forward by Bruner and Dluska (*loc. cit.*) and by Bancroft (Abstr., 1908, ii, 788), who suppose that the molecules of bromine attack the side-chain, whilst the atoms bring about substitution in the benzene nucleus, cannot, however, be sustained, inasmuch as a repetition of Cohen's experiments, using toluene and hydrogen bromide, showed that benzyl bromide and bromotoluene were both formed, but that the former underwent reduction by hydrogen produced in the electrolysis.

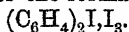
The suggestion is made that the true explanation is to be found in the existence of compounds of the type  $\text{HBr}_n$ , that these attack the benzene nucleus, whilst the molecules of bromine act only on the side-chain. This theory accounts satisfactorily for the influence of dilution, for the increase in the amount of benzyl bromide at higher temperatures, and for the increase in the proportion of bromotoluenes brought about by substances, such as acetic acid or nitrobenzene, which act as solvents for hydrogen bromide. An explanation is also afforded of the specific action of the bromides of iron, aluminium, and antimony, which also promote substitution in the ring.

W. O. W.

Properties of Diphenyleneiodonium Hydroxide and of some of its Derivatives. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 580—583; *Gazzetta*, 1908, 38, ii, 619—629. Compare Abstr., 1907, i, 1021).—On treating diphenyleneiodonium

iodide with moist silver oxide, it yields the hydroxide,  $\text{C}_6\text{H}_5\text{I} > \text{C}_6\text{H}_5\text{O}$ , which is a strong base and could not be isolated, owing to the readiness with which it absorbs carbon dioxide from the air. In aqueous

solution the hydroxide is reduced by sodium amalgam, giving an almost quantitative yield of diphenyl:  $C_{12}H_8I \cdot OH + 2H_2 = C_{12}H_{10} + HI + H_2O$ . This decomposition indicates the slight stability of the heterocyclic ring containing carbon and iodine, which is confirmed by the quantitative change of diphenyleneiodonium iodide into *o*:*o*-di-iododiphenyl when it is heated for a short time at its melting point. Evidence has been obtained of the formation of a periodide,

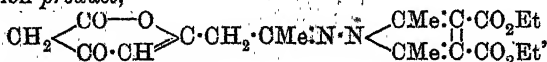


*Diphenyleneiodonium bromide*,  $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > I \cdot Br$ , separates from water as a white, crystalline powder, m. p. 245—250° (decomp.). When heated at its melting point, it is converted into 2-bromo-2'-iododiphenyl (?), m. p. 91.5°, which is under investigation. T. H. P.

**Action of *N*-Amino-compounds on Dehydracetic Acid.** CARL BÜLOW [with HANS FILCHNER] (*Ber.*, 1908, 41, 4161—4168).—Dehydracetic acid reacts with *p*-toluidine in alcoholic solution

to form *dehydracetic-p-toluidide*,  $CH_2 < \begin{matrix} CO-O \\ CO-CH \end{matrix} > C \cdot CH_2 \cdot CMe \cdot N \cdot C_7H_7$ , crystallising in colourless needles, m. p. 154°. Boiling with 10% sodium hydroxide resolves it into its components, again. It reacts with phenylhydrazine, *p*-toluidine being eliminated, and dehydracetic acid phenylhydrazone formed, crystallising in golden-yellow plates, m. p. 202°, and identical with the compound obtained by the direct interaction of phenylhydrazine and dehydracetic acid. It gives a characteristic blue coloration with concentrated sulphuric acid and a trace of ferric chloride, and is resolved on boiling with 10% sodium hydroxide into its components.

Ethyl-1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate condenses with dehydracetic acid in a similar manner to *p*-toluidine. The condensation product,



has m. p. 160°; it is of acid character, and dissolves in dilute alkali, whence it is precipitated by carbon dioxide.

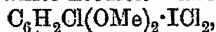
*Dehydracetic acid formylhydrazone*,  $C_8H_8O_3 \cdot N \cdot NH \cdot CHO$ , crystallises in colourless needles, m. p. 154°, and likewise possesses a faintly acid character.

*Dehydracetic acid semicarbazone*,  $C_8H_8O_3 \cdot N \cdot NH \cdot CO \cdot NH_2$ , crystallises in colourless needles, m. p. 197—198°; it dissolves in weak alkali, and is precipitated unchanged in crystalline form by weak acids.

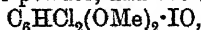
E. F. A.

**Chromophores without Double Linkings.** HUGO KAUFFMANN and IMMANUEL FRITZ (*Ber.*, 1908, 41, 4413—4422).—Ullmann and Loewenthal's 2-iodo-1:4-dimethoxybenzene (*Abstr.*, 1904, i, 725), m. p. 23°, b. p. 157°/10 mm., is conveniently obtained in 90% yield by treating an alcoholic solution of quinol dimethyl ether with iodine and mercuric oxide. A small quantity of *di-iodoquinol dimethyl ether*,  $C_6H_2I_2(OMe)_2$ , m. p. 171°, is also obtained. *Chloriodoquinol dimethyl ether*,  $C_6H_2ClI(OMe)_2$ , m. p. 115°, in which the position of the chlorine

has not been ascertained, is prepared by treating a chloroform solution of 2-iodo-1:4-dimethoxybenzene at 0° with chlorine, digesting the red product with 10% sodium hydroxide, and treating the resulting iodoso-compound with an acidified solution of potassium iodide; it separates from alcohol in white needles. The *iododichloride*,



m. p. 45—50° (decomp.), is a brick-red, crystalline powder, prepared by the action of chlorine on a chloroform solution of chloriodoquinol dimethyl ether at 0°; by treatment with 10% sodium hydroxide it yields a white, amorphous iodoso-compound,  $\text{C}_6\text{H}_2\text{Cl}(\text{OMe})_2 \cdot \text{IO}$ , m. p. 106° (decomp.). *Dichloriodoquinol dimethyl ether*,  $\text{C}_6\text{HCl}_2\text{I}(\text{OMe})_2$ , m. p. 81°, is obtained when the preceding iododichloride is kept in a closed vessel for some days, and separates from alcohol in white, woolly crystals; the *iododichloride*,  $\text{C}_6\text{HCl}_2(\text{OMe})_2 \cdot \text{ICl}_2$ , m. p. 130°, is a citron-yellow, crystalline powder, and the iodoso-compound,



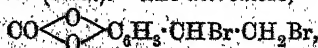
m. p. 70° (decomp.), is a white, amorphous substance.

*Trichloriodoquinol dimethyl ether*,  $\text{C}_6\text{Cl}_3\text{I}(\text{OMe})_2$ , m. p. 135°, crystallises in colourless needles, and is prepared by leading chlorine into a chloroform solution of 2-iodo-1:4-dimethoxybenzene, which is only slightly cooled, so that the final temperature is about 30°. The *iododichloride*,  $\text{C}_6\text{Cl}_3(\text{OMe})_2 \cdot \text{ICl}_2$ , m. p. 125—130° (decomp.), is a pale yellow, crystalline powder, and the iodoso-compound,  $\text{C}_6\text{Cl}_3(\text{OMe})_2 \cdot \text{IO}$ , m. p. 120—125°, prepared in the dark, is white and amorphous. *1:4-Dimethoxyphenyl di-iododichloride*,  $\text{C}_6\text{H}_2(\text{OMe})_2(\text{ICl}_2)_2$ , m. p. 50—60° (decomp.), prepared by leading chlorine into a chloroform solution of di-iodoquinol dimethyl ether at 0°, is an orange, crystalline powder, which by keeping for a few days in a closed vessel is converted into colourless *dichlorodi-iodoquinol dimethyl ether*. The *di-iodoso-compound*,  $\text{C}_6\text{H}_2(\text{OMe})_2(\text{IO})_2$ , is a yellow powder. C. S.

**Nitroquinol Dimethyl Ether.** HUGO KAUFFMANN (*Ber.*, 1908, 41, 4396—4412).—See this vol., ii, 107.

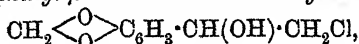
**Fluorescence of Potassium Quinoldisulphonate.** HUGO KAUFFMANN (*Ber.*, 1908, 41, 4422—4423).—In reply to Hantzsch (*Abstr.*, 1908, ii, 446), the author states that the fluorescence of potassium quinoldisulphonate, so far from being slight, is visible to the naked eye in an ordinary test-tube. C. S.

**Derivatives of Ethyl Catechol.** HERMANN PAULY and KARL NEUKAM (*Ber.*, 1908, 41, 4151—4161. Compare *Abstr.*, 1907, i, 916).—The dibromide of 3:4-dihydroxystyrene (vinylcatechol) methylene ether forms colourless, matted needles, m. p. 82° (compare Barger and Jowett, *Trans.*, 1905, 87, 967). When heated with bromine in carbon disulphide, a *tribromide*, m. p. 62°, crystallising in colourless needles, is formed. The cyclic carbonate,  $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH} \cdot \text{CH}_2$  (*Abstr.*, 1907, i, 916), exists in two forms: needles, m. p. 195° (corr.), and needles, m. p. 200° (corr.). The *dibromide*,



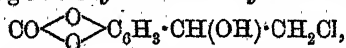
obtained by the action of bromine in carbon disulphide solution at  $-10^{\circ}$ , crystallises in short, obliquely-cut prisms, m. p.  $69-70^{\circ}$ . Free vinylcatechol is best prepared by hydrolysis of the carbonate with aqueous pyridine. It is obtained as a deep yellow, viscid oil, which easily polymerises; it dissolves in fuming hydrochloric acid with a rose-red coloration, which disappears on dilution. The view formerly expressed that vinylcatechol exists in a quinonoid form is now held with all reserve.

3 : 4-Dihydroxyphenyl- $\beta$ -chloro- $\alpha$ -ethanol methylene ether,



prepared by the addition of hypochlorous acid to the styrene, was obtained as a yellow oil, which on purification by distillation in a vacuum formed a colourless, odourless oil, b. p.  $157^{\circ}$  (corr.)/9 mm.,  $163-164^{\circ}$ /13 mm. When kept, the chlorine content increases, and  $\beta$ -chloro-methylenedioxystyrene,  $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH} : \text{CHCl}$ , is formed with the elimination of water. This is also formed on slow distillation of the chlorohydrin; it is a transparent, colourless oil with an anise or piperonaldehyde-like odour, b. p.  $138^{\circ}$ /11 mm.,  $141-142^{\circ}$ /13 mm. It forms an oily additive dibromide. At the same time as the above chlorohydrin, a substance containing an additional atom of chlorine is formed by the action of hypochlorous acid; this crystallises in well-formed, glistening, colourless needles, m. p.  $127.5^{\circ}$  (corr.). It shows no catechol reaction when heated with sodium carbonate.

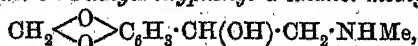
The corresponding chlorohydrin of the cyclic carbonate,



prepared in a similar manner, forms colourless crystals, m. p.  $95-96^{\circ}$ . The bromohydrin, prepared by the decomposition of the dibromide of vinylcatechol carbonate, separates in small, colourless prisms, which melt at  $100^{\circ}$  to a red liquid, and decompose to a greyish-violet dye, m. p. slowly heated  $96^{\circ}$ , or quickly heated,  $107^{\circ}$ . These carbonate derivatives give yellowish-brown colorations with ferric chloride.

The chlorohydrin of the catechol is obtained from the corresponding carbonate by heating with magnesium carbonate in acetone solution. The phenol is transferred to warm benzene, and quickly brought to crystallisation, using special precautions to prevent the formation of dyes. It crystallises in thin, colourless, pointed plates, m. p.  $102^{\circ}$ , decomposing instantly into a greyish-violet dye.

$\beta$ -Methylamino-3 : 4-dihydroxyphenyl- $\alpha$ -ethanol methylene ether,

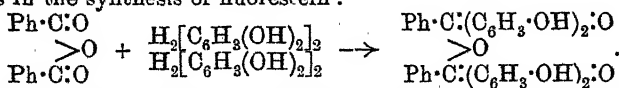


prepared by double decomposition of the chlorohydrin with methylamine, is a viscid, colourless oil with a faint violet fluorescence, b. p.  $170^{\circ}$ /12-13 mm. It turns litmus blue, and is perhaps identical with the methylalkamine described by Barger and Jowett (*loc. cit.*). The picrate forms small, yellow, sandy crystals, m. p.  $188^{\circ}$  (corr.) (Barger and Jowett give  $178^{\circ}$ ). It unites with phenylcarbimide in alcoholic solution, forming in the first place an easily soluble oil, and subsequently, a crystalline compound, m. p.  $155^{\circ}$ , probably a hydrothiazole.

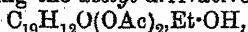
The carbonate of the chlorohydrin forms an amorphous base with methylamine very similar to epinephrine (Abel, Abstr., 1900, i, 72).

E. F. A.

**Resorcinolbenzein.** HANS VON LIEBIG (*J. pr. Chem.*, 1908, [ii], 78, 534—543. Compare Abstr., 1908, i, 445; Kehrman and Dengler, Abstr., 1908, i, 1002; Doebner, Abstr., 1883, 861; Cohn, Abstr., 1894, i, 120).—Resorcinolbenzein is formed by fusing resorcinol with either benzil or benzoic anhydride. It is possible that in the latter case a reaction takes place similar to that which occurs in the synthesis of fluorescein:



Resorcinolbenzein forms a *barium* salt,  $\text{C}_{76}\text{H}_{42}\text{O}_{12}\text{Ba}_4$ , glistening, bluish-red leaflets, and a *hydrochloride*,  $\text{C}_{76}\text{H}_{50}\text{O}_{12}\cdot 4\text{HCl}$ , brownish-yellow leaflets. It is converted by an alcoholic solution of ammonia into *anhydrosorcinolbenzein*,  $\text{C}_{76}\text{H}_{52}\text{O}_{12}$ ,  $\text{EtOH}$  (?), which crystallises in brownish-red leaflets with a blue shimmer. The latter compound and resorcinolbenzein, when boiled with glacial acetic acid, yield a *substance*,  $\text{C}_{76}\text{H}_{54}\text{O}_{14}\cdot\text{Ac}\cdot\text{OH}$ , obtained as brownish-red leaflets with a blue reflex. An alcoholic solution of potassium hydroxide converts resorcinolbenzein into a *substance*,  $\text{C}_{38}\text{H}_{20}\text{O}_9$ , almost colourless needles, m. p.  $147^\circ$  and 2:4:2':4'-tetrahydroxytritan-2:2'-ether,  $\text{C}_{19}\text{H}_{14}\text{O}_3$ , which crystallises with benzene of crystallisation in colourless leaflets or aggregates of prisms, m. p.  $170$ — $171^\circ$ . The latter substance is identical with Doebner's tetrahydroxytritan, which, however, because it was crystallised from dilute spirit, contained an additional  $\text{H}_2\text{O}$ . It yields an *acetyl* derivative,  $\text{C}_{19}\text{H}_{12}\text{O}(\text{OAc})_2$ , m. p.  $184^\circ$ , and a *dimethyl* derivative,  $\text{C}_{19}\text{H}_{12}\text{O}(\text{OMe})_2$ , thin, colourless leaflets, m. p.  $126^\circ$ . Resorcinolbenzein reacts with methyl sulphate, forming a *methyl* derivative,  $\text{C}_{19}\text{H}_{11}\text{O}(\text{OMe})_3$ , colourless crystals, m. p.  $105^\circ$ , and with acetic anhydride, yielding the *acetyl* derivative,



colourless, pointed prisms, m. p.  $147^\circ$ ; when the acetylation is carried out in the presence of zinc dust, the *acetyl* derivative,  $\text{C}_{38}\text{H}_{20}\text{O}_8(\text{OAc})_4$ , is formed; it crystallises in colourless, glistening needles, m. p.  $179^\circ$ .

W. H. G.

**The Structure of Guaiol.** A. GANDURIN (*Ber.*, 1908, 41, 4359—4363).—Guaiol (Wallach and Tuttle, Abstr., 1894, i, 538. Compare this vol., i, 112), extracted from guaiacum-wood oil by means of ether, crystallises from 70% alcohol in large, colourless prisms,  $[\alpha]_D^{25} -26.64^\circ$ ; it is triboluminescent. *Dihydroguaiene*, prepared by the action of zinc dust on guaiol, is a colourless, almost odourless oil, b. p.  $122^\circ/11$  mm.,  $[\alpha]_D^{25} -26.65^\circ$ ,  $D_4^{20} 0.9089$ ,  $D_4^{25} 0.8914$ ,  $n_D^{25} 1.49317$ . *Guaiol methyl ether* is a colourless, almost odourless oil, b. p.  $141$ — $143^\circ/9$  mm.,  $[\alpha]_D^{20} -31.81^\circ$ ,  $D_4^{20} 0.9513$ ,  $D_4^{25} 0.9332$ ,  $n_D^{25} 1.48963$ . *Guaiene*, prepared from guaiol through the xanthate (compare Wallach and Tuttle, *loc. cit.*), is a colourless, almost odourless oil, b. p.  $124^\circ/11$  mm.

$[\alpha]_D^{25} - 66.11^\circ$ ,  $D_4^{20} 0.9133$ ,  $D_5^{25} 0.8954$ ,  $n_D^{25} 1.49468$ . The author draws the conclusion, particularly from the mol. refraction of the above substances, that gualol is a tertiary dicyclic alcohol containing an ethylene linking.

J. C. C.

**Triphenylcarbinols.** HUGO KAUFFMANN and IMMANUEL FRITZ (*Ber.*, 1908, 41, 4423—4427. Compare *Abstr.*, 1905, i, 280, 773).—2-Iodo-1:4-dimethoxybenzene readily reacts with magnesium in dry ether, and the reaction of the oily product with ethereal 2:5-dimethoxybenzophenone leads to the formation of 2:5:2':5'-tetramethoxytriphenylcarbinol,  $\text{OH}\cdot\text{CPh}[\text{C}_6\text{H}_3(\text{OMe})_2]_2$ , m. p.  $120^\circ$ , which develops a dark green colour with concentrated sulphuric acid, and is reduced by warm alcoholic hydrogen chloride to 2:5:2':5'-tetramethoxytriphenylmethane, m. p.  $74^\circ$ . The ethereal solution of the preceding organo-magnesium compound reacts with carbon dioxide, yielding in the usual way a small amount of dimethylgentisic acid and, as the main product, Kauffmann and Grombach's 2:5:2':5'-tetramethoxybenzophenone. The interaction of the latter and the organo-magnesium compound leads to the formation of 2:5:2':5':2'':5''-hexamethoxytriphenylcarbinol,  $\text{OH}\cdot\text{C}[\text{C}_6\text{H}_3(\text{OMe})_2]_3$ , m. p.  $136^\circ$ , which gives an indigo-blue coloration with concentrated sulphuric acid, a green coloration with concentrated hydrochloric acid, and yields by reduction with alcoholic hydrogen chloride or with zinc and glacial acetic acid, 2:5:2':5':2'':5''-hexamethoxytriphenylmethane, m. p.  $151^\circ$ .

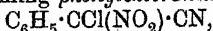
C. S.

**Electrolytic Reduction of Benzoic and Salicylic Acids to the Corresponding Aldehydes.** CARL METTLER (*Ber.*, 1908, 41, 4148—4150).—Benzoic acid in presence of mineral acids is electrolytically reduced to the corresponding alcohol (*Abstr.*, 1905, i, 436; 1906, i, 851; 1907, i, 315), and no trace of aldehyde is formed during the reaction. In neutral or alkaline solution, hydrogenated carboxylic acids are formed. On reduction, however, in presence of boric acid, considerable quantities of aldehyde are formed (compare Weil, *Abstr.*, 1908, i, 800). It is convenient to use an aqueous boric acid solution and sodium benzoate with a mercury cathode, which gives rise to sodium amalgam on passing the current, and this reduces the benzoic acid to aldehyde. It is necessary to ensure the continued presence of boric acid and to remove the aldehyde formed from further reducing action. To this end benzene is added, and the liquid stirred rapidly to keep it in a constant state of emulsion. Benzoic and salicylic acids and some of their derivatives can be reduced to aldehyde in this manner; the reaction takes place only with difficulty in the case of the halogen benzoic acids and of hydroxynaphthoic acid.

E. F. A.

**Preparation of Benzoyl Cyanide.** WILHELM WISLICHENUS and ROBERT SCHÄFER (*Ber.*, 1908, 41, 4169—4171).—It has previously been shown (*Abstr.*, 1908, i, 973; this vol., i, 29) that the group  $\text{C}(\text{NO}_2)_2\text{Br}$  has a pronounced tendency to eliminate bromine and nitric oxide and form the keto-group. Phenylacetone nitrile is readily converted by means of ethyl nitrate and sodium ethoxide into the sodium

derivative of phenylisnitro-acetonitrile (Abstr., 1902, i, 541), which Flürsheim (Abstr., 1903, i, 79) has converted into bromocyano-phenylnitromethane. Chlorine acts on the acetonitrile even more readily than bromine, forming *phenylchloronitrocyanomethane*,



a light yellow oil. This rapidly decomposes when warmed, and affords almost the theoretical quantity of benzoyl cyanide, crystallising in large plates, m. p. 32—34°. Iodine is without action on phenylis-nitro-acetonitrile. E. F. A.

*l*-Campholic Acid. MARCEL GUERBET (*Compt. rend.*, 1909, 148, 98—101).—*l*-Campholic acid can be prepared by the method described previously for the dextro-acid (Abstr., 1908, i, 661). When *l*-borneol, identified with *l*-camphol by Haller's method (Abstr., 1889, 1206), is heated in sealed tubes with recently-fused potassium hydroxide, it is

oxidised thus:  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{OH} \end{smallmatrix} + \text{KOH} = \text{C}_8\text{H}_{14}\begin{smallmatrix} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CO}_2\text{K} \end{smallmatrix} + \text{H}_2$ . The

resulting *l*-campholic acid forms colourless crystals, m. p. 106—107°,  $[\alpha]_D^{15} - 49.1^\circ$  (molecular solution in 95% alcohol). Its chemical properties are similar to those of the *d*-acid (compare Guerbet, Abstr., 1896, i, 56). The ammonium salt readily dissociates, evaporation of its aqueous solution leaving the acid. It cannot be esterified by the direct action of alcohols with or without the presence of hydrogen chloride. *l*-Campholic anhydride,  $(\text{C}_{10}\text{H}_{17}\text{O})_2\text{O}$ , prepared by dehydrating the acid with acetic anhydride, crystallises from acetone in colourless, square tablets, m. p. 57—58°, which are not attacked by cold alcohol, but give ethyl campholate on boiling with the latter. It is gradually hydrolysed by boiling aqueous potash. The chloride,  $\text{C}_{10}\text{H}_{17}\text{OCl}$ , obtained by treating the acid with a slight excess of phosphorus pentachloride, is a colourless liquid, b. p. 222° (the same as the *d*-isomeride), which, when heated with a trace of phosphoric oxide, decomposes into hydrogen chloride, carbon monoxide, and *i*-campholene,  $\text{C}_9\text{H}_{16}$ . Ethyl *l*-campholate,  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{Et}$ , prepared by the action of alcohol on either the anhydride or the chloride, is a colourless, oily liquid, b. p. 228°/765 mm. (corr.), having a strong odour of pears. It is not saponified by alkalis under ordinary conditions, but is readily decomposed on heating with hydriodic acid.

The sodium salt,  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{Na}\cdot 8\text{H}_2\text{O}$ , crystallises in efflorescent, nacreous lamellae, whilst the copper salt,  $(\text{C}_{10}\text{H}_{17}\text{O}_2)_2\text{Cu}\cdot\text{OEt}_2$ , crystallises from ether in large, green prisms containing ether of crystallisation.

*l*-Campholamide, obtained by the action of ammonia on an ethereal solution of the chloride, forms colourless needles, m. p. 77—78°, which are difficultly hydrolysed by alkalis, but readily by acids. E. H.

Syntheses in the Camphor Group. I. *iso*Laurolene and *iso*Lauronolic Acid (*β*-Campholytic Acid). GUSTAVE BLANC (*Bull. Soc. chim.*, 1909, [iv], 5, 24—31).—A résumé in greater detail of results already published (Abstr., 1906, i, 523) dealing with the syntheses of these two substances from *αα*-dimethyladipic acid as a starting point.

The product of the condensation of isolaurelene with acetyl chloride in presence of aluminium chloride (Abstr., 1899, i, 630; 1906, i, 524) contains a substance which is probably *tetrahydro-p-xylyl methyl ketone*, b. p. 210°. This is liquid, and yields an *oxime*, m. p. 106°, crystallising in small prisms, and sparingly soluble in light petroleum. The principal product of the condensation is the

ketone,  $\begin{array}{c} \text{CMe}_2 \cdot \text{CMe}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{CH} \cdot \text{COMe}$  (*loc. cit.*), which yields an *oxime*,

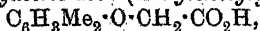
m. p. 65°, readily soluble in light petroleum, and with care can be oxidised directly by sodium hypobromite to isolauronolic acid, or the ketone may be reduced by sodium in alcohol to the secondary alcohol,  $\begin{array}{c} \text{CMe}_2 \cdot \text{CHMe}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > \text{CH} \cdot \text{CHMe} \cdot \text{OH}$  (*loc. cit.*), which, on oxidation with

chromic acid, is converted into 3-acetyl-1:1:2-trimethylcyclopentane, b. p. 195°, a mobile liquid with a faint odour; its *semicarbazone*, m. p. 213°, is sparingly soluble in alcohol, and the *oxime*, m. p. 47°, b. p. 137°/20 mm., forms large scales, and is readily soluble in most organic solvents. This ketone is oxidised by nitric acid, or, better, by sodium hypobromite solution, to dihydroiselauronolic acid, and this, on bromination and treatment with potassium hydroxide in alcohol, yields iselauronolic acid, as described already (Abstr., 1906, i, 524).

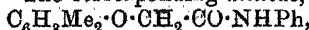
T. A. H.

**Xylenolglycollic [Dimethylphenoxyacetic] Acids and their Derivatives.** GIOVANNI JANDOLO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 149—155).—These acids may be obtained in good yield by melting the xylenols with chloroacetic acid, and adding a quantity of sodium hydroxide solution (1.3) three times as great as that of the xylenol used.

2:4-Dimethylphenoxyacetic acid (*m-xylenolglycollic acid*),



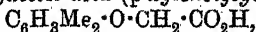
crystallises from all the ordinary solvents in flat, white needles, m. p. 141°. Its *silver*,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{Ag}$ , and *barium*,  $(\text{C}_{10}\text{H}_{11}\text{O}_3)_2\text{Ba} \cdot 2\text{H}_2\text{O}$ , salts were prepared. The corresponding *anilide*,



crystallises from alcohol in a silky mass of slender needles, m. p. 104°. The *anhydride*,  $(\text{C}_{10}\text{H}_{11}\text{O}_3)_2\text{O}$ , crystallises from alcohol in yellow needles, m. p. 94—95°.

$\alpha$ -2:4-Dimethylphenoxyacetic acid (*m-xylenolcinnamic acid*),  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{O} \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{CHPh}$ , crystallises from alcohol in transparent, white prisms, m. p. 171°. The *barium* and *silver* salts were prepared.

2:5-Dimethylphenoxyacetic acid (*p-xylenolglycollic acid*),

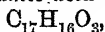


crystallises from water in transparent, white needles, m. p. 119°. The *silver* and *barium* (+2H<sub>2</sub>O) salts were prepared. The *anilide*,  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from alcohol in groups of white, silky needles, m. p. 90°.

3:4-Dimethylphenoxyacetic acid (*o-xylenolglycollic acid*),  $\text{C}_{10}\text{H}_{12}\text{O}_3$ , crystallises in shining, white scales, m. p. 162°. The *silver* and

barium ( $2\text{H}_2\text{O}$ ) salts were prepared. The anilide,  $\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}$ , forms colourless, rectangular, monoclinic laminæ, m. p.  $80^\circ$ .

$\alpha$ -3 : 4-Dimethylphenoxycinnamic acid (*o*-xylenolcinnamic acid),

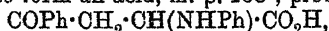


forms white prisms, m. p.  $180^\circ$ .

Attempts to prepare  $\alpha$ -2 : 5-dimethylphenoxycinnamic acid (*p*-xylenolcinnamic acid) did not result in a pure product, owing to the difficulty of crystallising it.

T. H. P.

**Benzoylacrylic Acid.** J. BOUGAULT (*Ann. Chim. Phys.*, 1908, [viii], 15, 491—515).—A detailed account of the preparation and properties of benzoylacrylic acid and its derivatives, part of which has been already published (Abstr., 1908, i, 179, 269, 422, 537, 791). Benzoylacrylic acid, more conveniently prepared from  $\beta$ -bromobenzoylpropionic acid by the action of sodium acetate and acetic acid (Wolff, Abstr., 1891, 1185), combines with bromine to form the dibromo-derivative, m. p.  $148^\circ$  (Pechmann, Abstr., 1882, 1074, gives  $135^\circ$ ). When treated with ammonia, benzoylacrylic acid yields the ammonium salt, m. p.  $197^\circ$ , of an amino-acid, which probably has the constitution  $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , whilst with aniline it combines directly to form an acid, m. p.  $138^\circ$ , probably

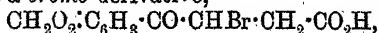


which condenses with phenylhydrazine to form the acid,  $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}_3$ , m. p.  $151^\circ$ .

The compound obtained by Gabriel and Colman (Abstr., 1899, i, 390) by the interaction of hydrazine and benzoylacrylic acid is probably not the hydrazone as described, but 3-phenylpyrazoline-5-carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{CH}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ | \\ \text{CH}_2\cdot\text{CPh} \end{smallmatrix}$ , which yields the crystalline bromo-

derivative,  $\text{CO}_2\text{H}\cdot\text{CH}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ | \\ \text{CHBr}\cdot\text{CPh} \end{smallmatrix}$ , m. p.  $251^\circ$ . The oxime and semi-

carbazone of benzoylacrylic acid have m. p.  $168^\circ$  and  $190^\circ$  respectively. *p*-Methoxy- and methylenedioxy-benzoylacrylic acids (Abstr., 1908, i, 269) can also be prepared by the action of sodium acetate and acetic acid on the bromo-derivative of *p*-methoxybenzoylpropionic acid and methylenedioxybenzoylpropionic acid respectively. *p*-Methoxybenzoylpropionic acid (anisoylpropionic acid) has m. p.  $147^\circ$  (Poppenberg, Abstr., 1902, i, 60, gives  $140$ — $141^\circ$ ); the bromo-derivative,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , has m. p.  $114^\circ$ ; methylenedioxybenzoylpropionic acid,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $136^\circ$ , yields a bromo-derivative,



m. p.  $147^\circ$ .

M. A. W.

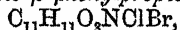
**The Colours of Indoneacetic Acids and their Carbazones.** HANS STOBEE and OTTO HORN (*Ber.*, 1908, 41, 4381—4384).—The colours of indoneacetic acid (this vol., i, 31), 3-methyl-1-indone-2-acetic acid (Abstr., 1904, i, 503), and 3-phenyl-1-indone-2-acetic acid (*ibid.*, 1902, i, 542), and of their semicarbazones, have been examined, and their ultra-violet absorption spectra photographed.

The substitution of methyl for hydrogen in either the acid or its semicarbazone has no effect on the colour, whereas introduction of phenyl increases the depth of the colour, the absorption limit of the phenylated acid being 34 wave-lengths nearer the red end of the spectrum. The relationships are much the same in the case of the semicarbazones (compare Abstr., 1906, i, 960).

All three semicarbazones are paler in colour than the corresponding acids. J. J. S.

Mode of Oxidation of Phenyl Derivatives of Fatty Acids in the Animal Organism. III. Synthesis of some Derivatives of Phenylpropionic Acid. HENRY D. DAKIN (*J. Biol. Chem.*, 1908, 5, 303—309. Compare Abstr., 1908, ii, 720, 964).—In the organism,  $\beta$ -hydroxy- $\beta$ -phenylpropionic acid is oxidised with much greater difficulty than  $\beta$ -phenylpropionic acid, and is mostly excreted unchanged. In order to test the hypothesis that combination with glycine is a necessary preliminary to combustion,  $\beta$ -hydroxy- $\beta$ -phenylpropionylglycine,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{H}$ , was prepared.

Cinnamoylglycine,  $\text{C}_{11}\text{H}_{11}\text{O}_3\text{N}$ , obtained by the Schotten-Baumann reaction, was found to be identical with that previously obtained from urine (*loc. cit.*), and yielded successively  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionylglycine,  $\text{C}_{11}\text{H}_{11}\text{O}_3\text{NBr}_2$ , prisms, m. p. 190—191°,  $\alpha$ -bromo- $\beta$ -hydroxy- $\beta$ -phenylpropionylglycine,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{NBr}$ , needles, m. p. 87—88°, and  $\beta$ -hydroxy- $\beta$ -phenylpropionylglycine,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$ , needles, m. p. 146—147°. The last substance but one, yields with warm concentrated hydrochloric acid,  $\beta$ -chloro- $\alpha$ -bromo- $\beta$ -phenylpropionylglycine,



m. p. 203—204°.

G. B.

*iso*Phthalacene Group: Structure of Phthalacene. II. GIORGIO ERRERA (*Gazzetta*, 1908, 38, ii, 588—598. Compare Abstr., 1908, i, 183).—The author has investigated the structure of the acids obtained by the action of concentrated sulphuric acid on 3:5-diphenyltoluene-2:2':2"-tricarboxylic acid (*loc. cit.*). It is found that this action yields the following three isomeric monobasic acids, which were separated by means of their ethyl esters: (1) the original phthalacene-carboxylic acid, which yields 3:5-diphenyltoluene-2:2':2"-tricarboxylic acid when fused with potassium hydroxide; (2) *isophthalacene*-carboxylic acid, which when reduced with hydriodic acid and phosphorus yields (a) an isomeride of phthalacene to which the name *iso*-phthalacene is given, and (b) *isophthalacene*-carboxylic acid; (3) *phthalaceneisocarboxylic acid*. The oxidation of *isophthalacene* yields the oxide of *isophthalacene* and *isophthalacene*, which are analogous with the corresponding oxidation products of phthalacene.

*Ethyl isophthalaceneisocarboxylate*,  $\begin{array}{c} \text{CO}-\text{C}(\text{OMe})-\text{C}(\text{CO}) \\ | \\ \text{C}_6\text{H}_4\cdot\text{C}(\text{CH})-\text{C}(\text{C}_6\text{H}_5-\text{CO}_2\text{Et}) \end{array}$  crystallises from acetic acid in shining, golden-yellow needles, m. p. 316°, and dissolves sparingly in alcohol or benzene and readily in xylene. The corresponding acid,  $\text{C}_{22}\text{H}_{12}\text{O}_4$ , separates from xylene or acetic acid in minute, irregular, brownish-yellow crystals, m. p. 370° (decomp.), and dissolves sparingly in the ordinary solvents.

*Ethyl phthalaceneisocarboxylate*,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} : \text{CH} \cdot \text{CMe} : \text{C} : \text{CO} \\ \text{CO} - \text{C} = \text{C} = \text{C} \cdot \text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Et} \end{array}$  is deposited from xylene in shining, golden-yellow crystals, m. p. 329—330°.

*isoPhthalaceneisocarboxylic acid*,  $\begin{array}{c} \text{CH}_2 - \text{C} : \text{CMe} : \text{C} : \text{CH}_2 \\ \text{C}_6\text{H}_4 \cdot \text{C} : \text{CH} - \text{C} \cdot \text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H} \end{array}$  crystallises from acetic acid in faintly yellow leaflets or needles, m. p. 286—287°, and dissolves sparingly in alcohol, benzene, or xylene. The *ethyl ester*,  $\text{C}_{24}\text{H}_{20}\text{O}_3$ , separating from acetic acid as a dirty yellow, crystalline powder, m. p. 172—173°, and the *sodium salt*,  $\text{C}_{22}\text{H}_{15}\text{O}_2\text{Na} \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , were prepared.

*isoPhthalacene*,  $\begin{array}{c} \text{CH}_2 - \text{C} : \text{CMe} : \text{C} : \text{CH}_2 \\ \text{C}_6\text{H}_4 \cdot \text{C} : \text{CH} - \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$ , crystallises from benzene in faintly yellow laminae, m. p. 222°.

*isoPhthalacene oxide*,  $\begin{array}{c} \text{CO} - \text{C} : \text{CMe} : \text{C} : \text{CH}_2 \\ \text{C}_6\text{H}_4 \cdot \text{C} : \text{CH} - \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$ , crystallises from acetic acid in golden-yellow leaflets, m. p. 216—218°.

*isoPhthalacene*,  $\begin{array}{c} \text{CO} - \text{C} : \text{CMe} : \text{C} : \text{CO} \\ \text{C}_6\text{H}_4 \cdot \text{C} : \text{CH} - \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$ , crystallises from aniline in shining, golden-yellow needles, m. p. 355—356°. T. H. P.

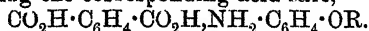
**Hydrophthalic Acids; Velocity of Addition of Bromine to the Tetrahydrophthalic Anhydrides.** VI. GINO ABATI [with MAURO SOLIMENE] (*Gazzetta*, 1908, 38, ii, 577—587. Compare Abstr., 1907, i, 419, 420).—The author has investigated the rate of addition of bromine (0.01 mol. solution) to each of the five tetrahydrophthalic anhydrides dissolved in chloroform (0.01 mol. solution) at 25°.

Bauer (Abstr., 1905, i, 729; 1907, i, 307) finds that the accumulation of negative substituent groups at two carbon atoms connected by an ethylene linking diminishes or annuls the capacity of the compound to unite with bromine. This is in accord with the author's observation that the  $\Delta^1$ -tetrahydrophthalic anhydride requires thirty-four days to complete the addition of bromine, whilst with the *cis*- $\Delta^4$ -anhydride less than three days is required; with the other anhydrides examined, no such relation is observed. There appears to be a close connexion between the time occupied by the anhydride in absorbing bromine and the dissociation constant of the corresponding acid, as is seen from the following table:

	Time of absorption of bromine.	Dissociation constant of acid.
$\Delta^1$ -Anhydride .....	33—34 days	0.0590
$\Delta^3$ -Anhydride .....	25—26 "	0.0581
<i>trans</i> - $\Delta^4$ -Anhydride .....	20—21 "	0.0118—0.0180
$\Delta^4$ -Anhydride .....	14—15 "	0.0074
<i>cis</i> - $\Delta^4$ -Anhydride .....	2—3 "	0.0062

The conclusion is drawn from these and other results that the unsaturated carbon atoms constituting the ethylene linking are of such a nature that the influences tending to lower the capacity of the linking to take up a negative element tend to increase the capacity of addition of a positive element, and vice versa. T. H. P.

Action of *iso*Phthalic and Terephthalic Acids on *p*-Aminophenols. DOMENICO PUGLIESE and GIAMBATTISTA SELVAGGI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 141—146).—In alcoholic solution, *isophthalic* acid (1 mol.) and *p*-aminophenol or its ethers (1 mol.) react, giving the corresponding acid salt,



With terephthalic acid, however, no reaction takes place, probably owing to the slight solubility and feeble acid properties of the acid.

When, however, *isophthalic* or terephthalic acid (1 mol.) and a *p*-aminophenol ether (1 or 2 mols.) are heated together in the absence of a solvent, they react, giving only the corresponding diamide:  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2 + 2\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OR} = \text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OR})_2 + 2\text{H}_2\text{O}$ . In some instances, however, further changes went on to such an extent, even when the compounds were heated together in a stream of carbon dioxide, that the diamide could not be separated in quantity sufficient for analysis.

*p*-Anisidine hydrogen *isophthalate*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , separates in shining, white fragments, and begins to turn brown without melting at above  $200^\circ$ .

*p*-Phenetidine hydrogen *isophthalate*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , is deposited in tufts of white needles, and decomposes at slightly above  $100^\circ$ .

*isoPhthalodi-p-anisidide*,  $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , prepared by the interaction of *isophthalic* acid (1 mol.) and *p*-anisidine (2 mols.), crystallises from alcohol in slender, neutral, white needles, m. p.  $268^\circ$ .

*Terephthalodi-p-anisidide*,  $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , crystallises from alcohol in neutral nacreous scales, m. p.  $246\text{--}248^\circ$ .

*Terephthalodi-p-phenetidide*,  $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , prepared from terephthalic acid and *p*-phenetidine, was obtained mixed with terephthalic acid, which could not be removed by crystallisation.

T. H. P.

Phenylitaconic Acid. HANS STOBBE (*Ber.*, 1908, 41, 4350—4357).—The author has made a further study of the reaction between ethyl succinate and benzaldehyde (Stobbe and Klöppel, *Abstr.*, 1894, i, 594) with the object of obtaining an increased yield of phenylitaconic acid (compare Hecht, *Abstr.*, 1903, i, 700). The anhydride and the two mono-esters have also been investigated.

[With OTTO HORN].—Phenylitaconic acid is obtained in a 35% yield by adding slowly a mixture of ethyl succinate and benzaldehyde to finely-divided sodium ethoxide suspended in boiling ether, and boiling the whole for three hours. The sodium salts of dibenzylidene-succinic, phenylitaconic, and phenylaticonic acids are separated by crystallisation and extraction with water. Phenylitaconic anhydride is readily obtained by treating the acid with cold acetyl chloride. The  $\beta$ -ethyl ester,  $\text{CHPh}\cdot\text{C}(\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{CO}_2\text{Et}$  (Fittig and Leoni, *Abstr.*, 1890, 894), crystallises in needles or tablets, m. p.  $72^\circ$ . The barium, calcium, and silver salts are described.

[With PHOKION NAOM.]—The  $\alpha$ -ethyl ester (Fittig and Leoni, *loc. cit.*) forms hairy, woolly needles, m. p.  $76\text{--}79^\circ$ .

J. C.

**Iminodicarboxylic Acids.** GEORGE STADNIKOFF (*Ber.*, 1908, 41, 4364—4373; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1638—1649).—The author finds that the rate of formation of derivatives of iminoacids decreases with increase of the molecular weight of the hydroxynitrile, but has no relation to the molecular weight of the amino-ester. Both in the synthesis of the iminoacids previously described (*Abstr.*, 1907, i, 393, 1015, 1016) and in the interaction of hydroxypropionitrile and ethyl aminocycloheptanecarboxylate or phenylaminoacetic acid, the reaction is at an end in five hours, whilst the interaction of mandelonitrile and ethyl aminoacetate or phenylaminoacetate requires ten days for completion; it is, however, quicker in the sunlight than in the dark.

*C-Phenyliminodiacetic acid*,  $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by condensing the hydrochloride of glycine ethyl ester with benzaldehyde and potassium cyanide, and hydrolysing the resulting *nitrile hydrochloride* (m. p.  $82^\circ$  decomp.), crystallises in starry aggregates of small needles, m. p.  $220^\circ$  (decomp.); the *hydrochloride* forms leaflets, m. p.  $220^\circ$  (decomp.); the *copper salt* ( $3\text{H}_2\text{O}$ ) is described. The *diethyl ester* is a colourless oil with a faint odour, b. p.  $195\text{--}196^\circ/17\text{ mm.}$ ; the *nitroso-derivative* of the latter is a yellow, viscid oil, b. p.  $220\text{--}221^\circ/17\text{ mm.}$  The *dimethyl ester* is a viscid oil, b. p.  $188\text{--}189^\circ/17\text{ mm.}$ , and yield a *nitroso-derivative*, which is a viscid, yellow oil, b. p.  $201\text{--}203^\circ/16\text{ mm.}$

sym.-*C-Phenyl-C-methyliminodiacetic acid*,



prepared by the interaction of ethyl phenylaminoacetate hydrochloride, acetaldehyde, and potassium cyanide, and hydrolysis of the resulting *nitrile hydrochloride* (m. p.  $160\text{--}161^\circ$  decomp.), crystallises in starry aggregates of slender needles, decomp.  $210\text{--}213^\circ$ ; the *hydrochloride* has m. p.  $210\text{--}212^\circ$  (decomp.), and the *diethyl ester* forms a viscid oil, b. p.  $182\text{--}183^\circ/13\text{ mm.}$

By the condensation of ethyl phenylaminoacetate hydrochloride, benzaldehyde, and potassium cyanide, the *hydrochloride* of the *nitrile ester*,  $\text{CO}_2\text{Et}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CN}\cdot\text{HCl}$ , is formed in slender needles, m. p.  $156\text{--}157^\circ$ ; with water it gives the *nitrile ester*, a crystalline mass, m. p.  $43\text{--}45^\circ$ . On boiling this with 20% hydrochloric acid, it is decomposed into phenylaminoacetic acid, benzaldehyde, and hydrogen cyanide.

J. C. C.

**Synthesis and Reactions of Ethyl Phloroglucinoldicarboxylate.** Condensation of Esters containing Nitrogen and the Preparation of Sodium Cyanate. HERMANN LEUCHS and ARTHUR GESERICK (*Ber.*, 1908, 41, 4171—4186).—The supposed ethyl phloroglucinoltricarboxylate synthesised by Baeyer by the sodium condensation of ethyl malonate was shown by Moore (*Trans.*, 1904, 85, 165) to be in reality ethyl phloroglucinoldicarboxylate. Willstätter (*Abstr.*, 1899, i, 576) isolated ethyl acetonetricarboxylate as an intermediate product, and observed the formation of ethyl acetate, which he attributed to the action of sodium ethoxide on ethyl malonate,  $\text{CH}_2(\text{CO}_2\text{Et})_2 + \text{EtOH} = \text{CH}_3\cdot\text{CO}_2\text{Et} + \text{CO}_2\text{Et}_2$ . He was to confirm the presence of ethyl carbonate, but this the

authors have succeeded in doing. The Baeyer synthesis is explained thus: two molecules of ethyl malonate unite to form ethyl acetone-tricarboxylate, which in turn reacts with ethyl acetate.

Ethyl malonate in cold ethereal solution is half converted into the sodium salt, the ether distilled off, and the residue heated at 130—140°, any liquid which distils being collected. A yellow, semi-solid mass is obtained, which, after purification, yields colourless needles of ethyl phloroglucinoldicarboxylate, m. p. 107—108.5° (corr.). Ethyl carbonate was obtained in quantity on fractionating the distilled liquid.

Ethyl malonate dissolved in light petroleum reacts with aluminium chloride, forming colourless crystals of ethyl aluminomalonate, m. p. 97—98° (Tistshenko gives 94—95°: Abstr., 1900, i, 270). This is decomposed by neither alkalis nor acids.

By the action of nitric acid on ethyl phloroglucinoldicarboxylate, three products are obtained. A very characteristic bluish-violet coloration is at first produced. *Ethyl nitrophloroglucinoldicarboxylate*,  $\text{NO}_2 \cdot \text{C}_6(\text{OH})_3(\text{CO}_2\text{Et})_2$ , crystallises in colourless, six-sided plates or massive prisms, m. p. 120—121° (corr.). It is conveniently prepared by heating equal weights of carbamide and the phloroglucinol compound with concentrated nitric acid at 80°. *Ethyl 5-nitro-2:4:6-triacetoxybenzene-1:3-dicarboxylate* forms colourless, prismatic crystals, m. p. 94—95°.

*Nitrophloroglucinol*,  $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{NO}_2$ , prepared by heating the ester at 130—135° with potassium hydroxide, crystallises in long, sealing wax-red prisms, which become yellowish-red on heating, m. p. 186—187° (corr.).

*Ethyl aminophloroglucinoldicarboxylate* is obtained, by reducing the nitro-compound with zinc and hydrogen chloride, in the form of the *hydrochloride*, crystallising in colourless needles, m. p. 209° (corr., decomp.). The base separates in minute needles, m. p. 96—97°. When left during several days in dilute methyl-alcoholic solution, crystals separate, and the alcohol assumes a deep red colour.

The other products of the action of nitric acid on ethyl phloroglucinoldicarboxylate are citron-yellow and dark red in colour; they are isomeric, and are formed from two molecules of ester united by an imino-group. The red substance,  $\text{C}_{22}\text{H}_{21}\text{O}_{13}\text{N}$ , is regarded as a quinone derived from ethyl hexahydroxydiphenylaminetetracarboxylate; it has m. p. 164—165°. By the action of acetic anhydride, a mixture of substances is produced, one of which has m. p. 138—152°, and crystallises in orange-yellow needles. The quinone is reduced on prolonged boiling with alcohol, or by means of sulphurous acid, to a brown compound,  $\text{C}_{22}\text{H}_{21}\text{O}_{12}\text{N}$ , which, on heating, becomes bright red at 130°, and dark brown again near the melting point, 196—197° (corr.). The *acetate* crystallises in orange-yellow needles, m. p. 175—177°.

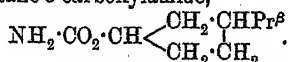
The *lactone* from ethyl hexahydroxydiphenylaminetetracarboxylate crystallises in citron-yellow needles, m. p. 220° (corr.); it forms a faintly yellow acetate, m. p. 169—171°, crystallising in needles.

The condensation of ethyl sodio-*N*-carbethoxyglycine yields an *ester*,  $\text{C}_{10}\text{H}_{14}\text{O}_6\text{N}_2$ , crystallising in long needles, m. p. 144—145° (corr.). This has an acid reaction in aqueous solution, and may be ethyl diketopiperazine-1-carboxylate or ethyl aminocyclobutan-2:4-dione-1:3-dicarboxylate.

Attempts to condense sodium urethane showed that reaction takes place between several molecules, but the intermolecular elimination of alcohol results in the quantitative formation of sodium cyanate. Similarly, the action of sodium on urethane in boiling benzene results in the formation of sodium cyanate alone. This is a convenient method for preparing salts of cyanic acid. E. F. A.

**Sodium Benzaldehydesulphoxylate. A Correction.** EMIL FROMM (*Ber.*, 1908, 41, 4385. Compare Abstr., 1908, i, 970).—When sodium benzaldehydesulphoxylate is heated with benzyl chloride and sodium hydroxide solution, the product is not the unaltered sulphoxylate as previously stated, but sodium benzylsulphonate. J. J. S.

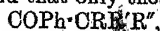
**Syntheses of Derivatives of Camphenilone.** J. BOUVEAULT and GUSTAV BLANC (*Compt. rend.*, 1908, 147, 1314—1315).—From previous work, the conclusion has been drawn (Abstr., 1908, i, 134) that the amide formed by the action of sodamide on camphenilone is *isopropylcyclopentane-3-carboxylamide*,



This conclusion is now verified by direct synthesis. *iso*Propylcyclopentan-3-one is obtained by the decomposition of  $\beta$ -*isopropyladipic* anhydride, and is shown to be identical with the ketone obtained from camphenilone, by preparation of its semicarbazone and its dibenzylidene derivative. On reduction with sodium and boiling alcohol, it gives a secondary alcohol, identical with that obtained from 3-amino-1-*isopropylcyclopentane* by the action of nitrous acid. This alcohol, when heated at 100° with hydrobromic acid, is transformed into 3-bromo-1-*isopropylcyclopentane*,  $\text{CHBr} \begin{array}{l} \text{CH}_2 \cdot \text{CHPr}^s \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$ , a heavy, colourless liquid, b. p. 82°/16 mm.

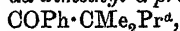
The latter reacts with Grignard's reagents, giving magnesium derivatives, which, when saturated with dry carbon dioxide, give 3-*isopropylcyclopentanecarboxylic acid*, identical with that derived from camphenilone. The acid, on treatment with phosphorus pentachloride and then with gaseous ammonia, readily furnishes the amide. E. H.

**A General Method of Preparing Mono-, Di-, and Tri-alkylacetophenones.** ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 148, 70—74).—It has been shown previously (Abstr., 1908, i, 987) that aromatic ketones of the type of benzophenone, when heated with sodamide in benzene solution, give either additive or decomposition products. The authors, attempting to apply this reaction to mixed fatty-aromatic ketones, find that only those of the type

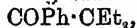


in which R, R', and R'' are alkyl groups, undergo the decomposition observed with diaryl ketones, that is, they break down into benzene and trialkylacetamides. Of the ketones employed, *aaa*-trimethylacetophenone,  $\text{COPh} \cdot \text{CMe}_3$ , has been described by Nef (Abstr., 1900, i, 349); the others were prepared by alkylating acetophenone in the presence

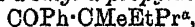
of sodamide, as in the method adopted with cyclic ketones (Haller, Abstr., 1904, i, 600; 1905, i, 214, 602), and by Claisen (Abstr., 1905, i, 236). *aa*-Dimethyl-*a*-ethylacetophenone,  $\text{COPh}\cdot\text{CMe}_2\text{Et}$ , obtained by twice methylating propiophenone or by ethylating phenyl isopropyl ketone, is a mobile, agreeably smelling liquid, b. p.  $112\text{--}5^\circ/10$  mm.; the *oxime* forms needles, m. p.  $139^\circ$ ; *aa*-dimethyl-*a*-propylacetophenone,



prepared by propylating phenyl isopropyl ketone, is a liquid with a penetrating odour, b. p.  $121\text{--}123^\circ/10$  mm.; its *oxime*, prepared by means of Crismer's reagent, crystallises in needles, m. p.  $132\text{--}133^\circ$ ; *a*-methyl-*aa*-diethylacetophenone,  $\text{COPh}\cdot\text{CMeEt}_2$ , an aromatic smelling liquid, b. p.  $125\text{--}126^\circ/11$  mm., results on twice ethylating phenyl ethyl ketone; the *oxime* has m. p.  $121^\circ$ ; *aaa*-triethylacetophenone,



obtained by successively ethylating acetophenone or by ethylating phenyl propyl ketone, is an agreeably smelling liquid, b. p.  $145\text{--}146^\circ/16$  mm.; the *oxime*, prepared with Crismer's reagent, forms needles, m. p.  $160\text{--}161^\circ$ ; *a*-methyl-*a*-ethyl-*a*-propylacetophenone,



prepared by successively methylating and propylating propiophenone, is a liquid, b. p.  $135\text{--}136^\circ/11$  mm., which forms an *oxime*, m. p.  $99\text{--}100^\circ$ ; *aa*-dimethyl-*a*-allylacetophenone,  $\text{COPh}\cdot\text{CMe}_2\cdot\text{C}_3\text{H}_5$ , a pleasant-smelling liquid, b. p.  $121^\circ/11$  mm., is formed by the action of allyl iodide on phenyl isopropyl ketone; its *oxime* could not be obtained.

By the action of propyl or allyl iodide on the additive product of sodamide and acetophenone, not substituted ketones, but condensation products of very high boiling point are formed; the higher homologues of acetophenone, however, undergo the normal reaction with these iodides.

E. H.

**Quinhydrone.** WILHELM SIEGMUND (*Monatsh.*, 1908, 29, 1087—1109. Compare Urban, Abstr., 1907, i, 539).—By the addition of light petroleum to a benzene solution of *p*-benzoquinone and catechol, a *quinhydrone*,  $\text{C}_{18}\text{H}_{16}\text{O}_6$ , m. p.  $90^\circ$  (decomp.),  $D_{20}^{20} 1.359$ , is obtained, which forms red needles, is stable in boiling benzene, and is decomposed by distillation with steam, yielding *p*-benzoquinone and catechol, the weight of the latter, estimated as the lead derivative, indicating that the quinhydrone contains 1 mol.  $\text{C}_6\text{H}_4\text{O}_2$  and 2 mols.  $\text{C}_6\text{H}_4(\text{OH})_2$ .

Quinol and  $\beta$ -naphthaquinone do not react in water, alcohol, ether, or benzene. In warm benzene, *p*-benzoquinone and 1:2-dihydroxynaphthalene yield, in the molecular proportion 1:1, quinol and  $\beta$ -naphthaquinone; in proportion 2:1,  $\beta$ -naphthaquinone and ordinary quinhydrone, and in the proportion 1:2, quinol and a bluish-black substance,  $\text{C}_{20}\text{H}_{18}\text{O}_4$ , m. p.  $120^\circ$ , which seems to be identical with Stenhouse and Grove's dinaphthylidiquinhydrone (*Trans.*, 1878, 33, 417).

The addition of light petroleum to a benzene solution of *p*-benzoquinone and 2:3-dihydroxynaphthalene produces tufts of blackish-red needles of the mixed *quinhydrone*;  $\text{C}_{16}\text{H}_{12}\text{O}_4$ .

The formulæ of the preceding quinhydrones are expressed in accordance with Thiele's theory of partial valencies. C. S.

**Complete Synthesis of Camphor.** GUSTAV KOMPPA (*Ber.*, 1908, 41, 4470—4474).—The synthesis of camphor from a compound containing a smaller number of carbon atoms described by Wallach recently (*Abstr.*, 1908, i, 997), is not the first synthesis of camphor to be recorded, since the author had previously synthesised racemic camphoric acid (*Abstr.*, 1901, i, 668; 1904, i, 141), which he was subsequently able to convert into racemic camphor (*Chem. Zeit.*, 1905, 29, 1202). It has since been found possible to obtain pure *l*-camphoric acid, but not pure *d*-camphoric acid, from the racemic acid by crystallisation of the quinine salts. Attempts are being made to resolve the racemic camphor into its components through the corresponding borneols. *r*-Campholide,  $C_{10}H_{16}O_2$ , prepared by the reduction of *r*-camphoric anhydride in alcoholic solution with sodium, or, better still, by means of nickel and hydrogen, crystallises in short, thick needles, m. p. 211·5—212° (corr.). It combines with hydrogen bromide, forming *r*-bromocampholic acid,  $C_{10}H_{17}O_2Br$ , rhombic plates, m. p. 178—179°, and when heated with potassium cyanide at 230—240° yields *r*-cyanocampholic acid, which is converted on hydrolysis into *r*-homocamphoric acid,  $C_9H_{16}(CO_2H)_2$ , obtained as feathery crystals, m. p. 231—232° (corr.). The calcium salt,  $C_{11}H_{16}O_4Ca \cdot 5H_2O$ , is a crystalline powder, which, when distilled with calcium hydroxide, yields *r*-camphor, m. p. 178—178·5° (corr.). W. H. G.

**Constituents of Ethereal Oils. Carvenene,  $C_{10}H_{16}$ , and "Pure" Terpinene.** FRIEDRICH W. SEMMLER (*Ber.*, 1908, 41, 4474—4479).—Emphasis is laid on the great differences in the physical properties of the "pure" terpenes obtained by various methods by the author (*Abstr.*, 1907, i, 714), Wallach (*Abstr.*, 1907, i, 64; 1908, i, 813), and Harries and Majima (*Abstr.*, 1908, i, 733). In order to throw some light, therefore, on the constitution of terpineine, the author has prepared pure carvenene by reducing chlorocarvenene, and finds that the hydrocarbon so obtained, which must have the formula  $CPr^s \begin{matrix} \text{CH} & \text{---} & \text{CH} \\ & \diagdown & / \\ & \text{CH}_2 & \text{---} & \text{CH}_2 \end{matrix} OMe$ , exhibits an exaltation of 1·5 units (compare Brühl, *Abstr.*, 1908, ii, 1002). It is thus definitely shown that two cyclic conjugate ethylene linkings produce a marked exaltation, consequently the two terpenes,  $\Delta^{1:3}$  and  $\Delta^{1:4}$ -dihydrocymene, must differ considerably in their physical constants. The identity of carvenene with terpinene has not yet been definitely settled.

The chlorocarvenene described by Klages and Kraith (*Abstr.*, 1900, i, 42) was impure. The pure substance has b. p. 95—98°/10 mm.,  $D_{20}^{25}$  0·994,  $n_D$  1·51700, and mol. ref. 51·90; that is, it exhibits an exaltation of 1·71 units. It is readily reduced by sodium and alcohol to carvenene, a colourless liquid, b. p. 61—63°/10 mm., 179·5—180·5°/735 mm.,  $D_{20}^{25}$  0·844, and  $n_D$  1·49100 (compare Harries and Majima, *loc. cit.*). The carvenene so prepared reacts slowly with nitrous acid, yielding terpinene nitrosite. W. H. G.

**Aliphatic Terpenes and their Derivatives. III. C. J. ENKLAAR** (*Rec. trav. chim.*, 1908, 27, 422—434. Compare Abstr., 1908, i, 664).—In the present communication the author describes the preparation and properties of the ozonides of ocimene (van Romburgh, Abstr., 1901, i, 220), *allo-ocimene*, and *dihydro-ocimene*. These ozonides are of somewhat variable composition, the amount of oxygen depending on the time during which the hydrocarbons are exposed to ozone.

*Ocimene ozonide*,  $C_{10}H_{16}O_9$ , occurs as a pale yellow, viscous oil, which explodes when heated or when brought into contact with concentrated sulphuric acid. When treated with water, decomposition occurs, with formation of acetone, acetic acid, malonic acid, methylglyoxal, and possibly malonaldehyde. *allo-Ocimene ozonide*,  $C_{10}H_{16}O_9$ , is an explosive oil rapidly decomposed by water with formation of acetone, pyruvic acid, and probably malonaldehyde.

*Dihydro-ocimene ozonide*, under the same conditions, gives acetone, acetic acid, lævulic acid, and probably lævulin aldehyde, and malonaldehyde. An insoluble yellow resin was also obtained in the decomposition of these ozonides by water; further treatment with ozone converts this into an ozonide.

A table is given showing the specific refractions for the  $\alpha$ - and  $\gamma$ -hydrogen lines and the *D*-sodium line, and also the molecular refractions for the different rays of these three hydrocarbons. The molecular dispersions between the  $\alpha$ - and  $\gamma$ -lines diverge considerably from the values calculated from Conrady's data. W. O. W.

**Ethereal Oils. HEINRICH HAENSEL** (*Haensel's Half-Yearly Report, October, 1908*. Compare Abstr., 1908, i, 665).—*Angelica oil* when free from terpene has  $D^{15}_D$  0.9508,  $\alpha_D$   $-3.16^\circ$ , acid number 0, ester number 87.3, after acetylation 168.1. *Oil of Mugwort*, from the fresh plant *Artemisia vulgaris* (yield 0.0263%), is dark brown and smells strongly aromatic;  $D^{20}_D$  0.9279. The addition of 90% alcohol causes separation of small, colourless plates, which give a decided aldehyde reaction with ammoniacal silver solution. *Birch-bark oil*, from *Betula alba*, has  $D^{20}_D$  0.9003,  $\alpha_D$   $-12.08^\circ$ , acid number 9.1, ester number 11.4, after acetylation 36.5. The sesquiterpene isolated from this was colourless and nearly odourless; it has b. p. 255—256°/744 mm.,  $D^{20}_D$  0.8844,  $\alpha_D$   $-0.5^\circ$ ; in glacial acetic acid it gives a cherry-red coloration with bromine, and combines with 1 mol. hydrogen chloride when in absolute ethereal solution. The resulting dark-coloured hydrochloride,  $D^{20}_D$  0.9753, when boiled with anhydrous sodium acetate and acetic acid, yields a hydrocarbon, b. p. 258—260°/747 mm.,  $D^{20}_D$  0.8898. *Coriander oil* (*loc. cit.*) is for the most part *d*-linalool, accompanied by small quantities of esters of this alcohol. *Cynoglossum oil*, prepared from the leaves of *Cynoglossum officinale* (yield 0.107%), is dark brown with powerful camomile-like odour; it partly solidifies when cooled, is soluble in all proportions of 90% alcohol, and has  $D^{20}_D$  0.9412. *Siberian pine needle oil*, from *Abies sibirica*, has  $D^{20}_D$  0.9767,  $\alpha_D$   $-38.30^\circ$ , soluble 1:14.2 in 63% alcohol.

*Guaiacum-wood oil* from *Bulnesia Sarmienti*.—Only about one-half of the guaiol contained in this oil is found by acetylation; it

appears to be a tertiary alcohol, in agreement with its behaviour towards phthalic anhydride. The guaiene obtained by warming the oil for an hour with three times its weight of anhydrous formic acid has b. p. 135—138°/14 mm.,  $D_{20}^{20}$  0.9182, and is most probably a mixture of sesquiterpenes (compare Gündurin, this vol., i, 98). *Oil of Lavender*, when free from terpene, has  $D_{20}^{20}$  0.8898,  $n_D^{20}$  1.44°, and is soluble 1:0.95 in 80% alcohol. *Oil of Lavage*, from *Levisticum officinale*, becomes slightly changed when kept; it then contains myristic acid, small quantities of an aldehyde possessing an odour resembling that of octaldehyde, and also larger quantities of a brown resin, which decomposes when warmed under reduced pressure. *Ginger-grass oil*, from *Andropogon Schoenanthus*, is optically inactive, has  $D_{20}^{20}$  0.8851, and dissolves in 3.5 parts of 60% alcohol. *Italian Peppermint oil*, crude and purified, has respectively  $D_{20}^{20}$  0.9035 and 0.9032,  $n_D^{20}$  -19.80° and -18.10°, ester number 11.2 and 9.1, after acetylation 154.4 and 145.9, content of esterified menthol 3% and 2.54%, content of free menthol 45.16% and 42.66%. *Hungarian oil of Juniper*.— $D_{20}^{20}$  0.8672,  $n_D^{20}$  -12°, saponification value 5.9, after acetylation 20.9, and contains according to the phthalic anhydride test about 5% of a primary alcohol,  $C_{10}H_{18}O$ . The Italian oil has  $D_{20}^{20}$  0.8658,  $n_D^{20}$  -9.82°, saponification value 6.1; after acetylation,  $D_{20}^{20}$  0.8732,  $n_D^{20}$  -7.21°, saponification value 21.3; after saponification and repeated acetylation a reversal of optical rotation appears to take place. In the higher boiling fractions, phthalic anhydride indicates the presence of small quantities of a primary alcohol,  $C_{10}H_{18}O$ ; the terpene fractions do not contain nopinene. *Olibanol from oil of Frankincense (loc. cit.)* has b. p. 217°/20 mm., 333—334°/751 mm.,  $D_{20}^{20}$  0.9596,  $n_D^{20}$  -71.50°; when warmed with an equal weight of molten zinc chloride, a dark green oil is obtained, b. p. 315—318°/749 mm.,  $D_{20}^{20}$  0.9400. *Olibanol* is only slightly oxidised by potassium permanganate in alkaline solution, but in glacial acetic acid solution it is completely oxidised by chromic acid. J. V. E.

**Essential Oils.** SCHIMMEL & Co. (*Semi-Annual Report*, Nov., 1908, 5—232. Compare Abstr., 1908, i, 666).—A résumé of information regarding essential oils accumulated during the period April to November 1908. Much of the matter recorded has appeared in other journals and has been abstracted already.

*Cinnamon-bark oil*.—Four samples from Mahé Islands, Seychelles, had  $D_{15}^{15}$  0.9464—0.9670,  $[\alpha]_D^{20}$  -2°30' to -5°10',  $n_D^{20}$  1.52843—1.53271, and contained from 25 to 35% of cinnamaldehyde and 6 to 15% "phenols." All the usual constituents of cinnamon-bark oil were present, and in addition a small amount of camphor (compare *Bull. Imp. Inst.*, 1908, 6, 111). *Clove-leaf oil*.—Clove leaves from the Seychelles yielded 4.5% of oil (*loc. cit.*); this had  $D_{15}^{15}$  1.0489,  $[\alpha]_D^{20}$  -1°35', eugenol 87%. *African Copaiba balsam* (oleo-resin) had  $D_{15}^{15}$  0.9919,  $[\alpha]_D^{20}$  -2°15', acid number 61.4, saponification number 68.5, and was not completely soluble in 98% alcohol. It contained 46.5% of volatile oil, having  $D_{15}^{15}$  0.9215,  $[\alpha]_D^{20}$  +22°26', and acid number 2.2. *Dalbergia cumingiana* oil, obtained to the extent of 0.5% from the wood, had  $D_{20}^{20}$  0.891,  $[\alpha]_D^{20}$  -4°31', ester number 5, acetyl ester number

115. No aldehydes were present (*Jaarboek Dept. Landb. Ned. Ind.*, 1906, 45). *Dill herb oil*, from Spanish herb, was greenish-blue, had  $D^{15}_D$  0.9062,  $n^{20}_D$  1.49185, and was dextrorotatory. It contained *d*- $\alpha$ -phellandrene, terpinene, carvone, dillapiol (? dilliscapiol), and dipentene or limonene (?).

*Lemon oil*.—The chief constants of oils from different districts in Sicily are recorded; they had  $D^{15}_D$  0.8569—0.8610,  $[\alpha]^{20}_D$  +56°50' to +62°40'; left from 2.2 to 3.6% residue on evaporation, and contained 4.3 to 7.1% citral. All these oils contained traces of pinene, which is a natural constituent of lemon oil. *Eucalyptus Rudderi* leaves and twigs furnished 0.309% of reddish-brown oil, having  $D^{15}_D$  0.942,  $[\alpha]_D$  -8.5°, and  $n^{20}_D$  1.4898. The oil contained cineol and aromadendral, but no pinene or phellandrene (Baker and Smith, *Proc. Linn. Soc., N.S.W.*, 1906, 31, 714). *European Wormseed oil* contains  $\alpha$ -pinene, terpinene, terpineol and terpinenol, and a sesquiterpene (b. p. 250° approx.) (compare Schindel-Meiser, *Apoth. Zeit.*, 1907, 22, 876). *Foeniculum officinale* stalks and leaves, grown in Java yielded an oil having  $D^{26}_D$  0.970,  $[\alpha]^{26}_D$  +4°50', b. p. 227—235°, m. p. 12.8°. A second sample of oil had  $D^{15}_D$  0.9837,  $[\alpha]_D$  +5°34', m. p. 16.2°. Both oils probably contain much anethole (*Jaarboek Dept. Landb. Ned. Ind.*, 1906, 45). *Hyptis suaveolens* oil from Java had  $[\alpha]_D$  -1°56' and saponification number 17. The yield was 1% and no aldehydes were present (*loc. cit.*, p. 46).

*Andropogon citratus* oil is contained in largest quantity in the leaves, and diminishes as the leaves age, becoming at the same time richer in citral. The leaf sheaths contain a little oil, and the thick roots 0.35 to 0.5%. A sample of "*Cochin China lemon grass*" oil produced in Barbados had  $D^{15}_D$  0.900,  $[\alpha]_D$  -1°, aldehydes 85.5 (neutral sulphite method). The "acid sulphite" and "neutral sulphite" processes for estimation of citral in lemon grass oil give results differing by from 2 to 5%, so that the process of estimation should always be stated. Methylheptenol has been detected in *linaloe* oil. *Monarda didyma* oil from the half-faded petals was pale yellow, and had  $D^{15}_D$  0.8665,  $[\alpha]_D$  -7°30',  $n^{20}_D$  1.46892, and acid number 2.4: the yield was 0.32%. The dry leaves and stems furnished 0.096% of a lemon-yellow, more soluble oil having  $D^{15}_D$  0.8855,  $[\alpha]_D$  -32°38',  $n^{20}_D$  1.46892, and acid number 5.5. Both oils had the odour of lavender.

*Nutmeg flowers* grown in Java yielded 7.6% of oil having  $D^{26}_D$  0.942,  $[\alpha]^{26}_D$  +7°, and b. p. 155—285°. Fresh nutmegs furnished 3.8% of oil having  $D^{26}_D$  0.940,  $[\alpha]^{26}_D$  +10°20', and b. p. 155—285° (de Jong "*Teysmannia*" 1907, 8). Condensed water from the distillation of *orris* root oil contained acetaldehyde, methyl alcohol, diacetyl, and furfuraldehyde. *Pastinaca* oil was found to contain heptioic and hexoic acids (*Apoth. Zeit.*, 1907, 22, 144). The physical constants of a number of Singapore and Java patchouli oils are recorded.

*Italian peppermint oil*, distilled from plants grown from Mitcham seed, had  $D^{15}_D$  0.9090,  $[\alpha]_D$  -21°12',  $n^{20}_D$  1.46248, and contained "total" menthol 50.5%, and menthone 17.2%. Java "*peppermint*" oil had  $D^{26}_D$  0.974,  $[\alpha]^{26}_D$  12°28', and "total menthol" 44.9% (*Jaarboek Dept. Landb. Ned. Ind.*, 1906, 45), but doubt is expressed as to the validity of the above composition.

*Poplar bud oil*.—Two samples had  $D^{15}$  0.8957 to 0.8991,  $[\alpha]_D + 5^\circ 16'$  to  $+5^\circ 45'$ , acid number 2.8–6.4, and ester number 8.2–8.9. Acetylation experiments showed that the oil contained but little "alcohols." *East African sandalwood oil*, from *Osyris tenuifolia*?—The yield from the wood was 4.86%. The oil had  $D^{15}$  0.9477,  $[\alpha]_D - 42^\circ 50'$ ,  $n_D^{20}$  1.52191, ester number 11.1, acetyl ester number 72.8. The odour recalled those of vetiver and gurjun balsam oils. *Thuja plicata*.—The leaves and twigs yielded 0.8 to 1.4% of bright yellow oil, which possessed a camphoraceous odour, and had  $D^{25}$  0.9305,  $[\alpha]_D^{25} - 6.9^\circ$ , acid number 0.518, saponification number 5.7, and acetyl ester number 6.2. It contained pinene, thujone, fenchone, and esters of borneol. *Ylang-ylang oil*, from Madagascar, had  $D^{15}$  0.9577,  $[\alpha]_D - 49^\circ 55'$ ,  $n_D^{20}$  1.51254, acid number 1.8, ester number 113.2, acetyl ester number 160.2. Samples from Mahé Island, Seychelles, had  $D^{15}$  0.924–0.958 and  $[\alpha]_D - 18^\circ 46'$  to  $45^\circ 27'$  (compare *Bull. Imp. Inst.*, 1908, 6, 110).

*Artemisia arborescens* yielded 0.62% of a dark blue oil, possessing an odour like that of French wormwood oil, and having  $D^{15}$  0.9458 and acid number 9.8. "Mumuta" grass tubers (*Andropogon*, sp.), from Samoa, gave 1.05% of an oil with an odour like that of vetiver oil, and having  $D^{15}$  0.9845,  $[\alpha]_D + 41^\circ 50'$ ,  $n_D^{20}$  1.51505, acid number 0.9, ester number 13.3, and acetyl ester number 65.2. From "Nuanua" leaves (*Nelitris*, sp.), from Samoa, 0.63% of oil was obtained. This had an odour like that of ambergris, and had  $D^{15}$  0.9025,  $[\alpha]_D + 9^\circ 30'$ ,  $n_D^{20}$  1.48490, acid number 2.2, and ester number 7.4. "Usi" leaves (*Evodia hortensis*), from Samoa, yielded 0.09% of a brown oil with a quinone-like odour, and had  $D^{15}$  0.9450,  $[\alpha]_D - 10^\circ$ , and  $n_D^{20}$  1.49685.

"Maali" resin, from Samoa, resembled elemi, and gave 16.08% of a bright green solid oil with a faintly balsamic odour. It had m. p.  $65-80^\circ$ ,  $[\alpha]_D + 7^\circ 15'$ , saponification number 3.3, and acetyl ester number 46.6. It contained *maalyi alcohol*,  $C_{15}H_{26}O$ , m. p.  $105^\circ$ ,  $[\alpha]_D + 18.33^\circ$ , b. p.  $260^\circ$  (approx.), which crystallised from alcohol in silky needles, often several inches in length, and formed with resorcinol a complex condensation product, m. p.  $62^\circ$ , and with chromic anhydride a red additive product,  $(C_{15}H_{26}O)_2 \cdot CrO_3$ , m. p.  $111^\circ$ . On treatment with acetic anhydride, or, better, formic acid, *maalyi alcohol* is converted into a *sesquiterpene*,  $C_{15}H_{24}$ ,  $D^{15}$  0.9190,  $[\alpha]_D + 121^\circ 20'$ ,  $n_D^{20}$  1.52252, b. p.  $270.8-271^\circ/754$  mm., which gives an indigo-blue coloration with sulphuric acid in acetic acid. No derivatives of the sesquiterpene could be prepared. The residue of the oil appears to consist of a solution of *maalyi alcohol* in a *lævotatory sesquiterpene*.

*Artemisia indica* (?), of Java, yielded 0.28% of a bright brown oil, having  $D^{20}$  0.949,  $[\alpha]_D^{20} + 57^\circ 2'$ , saponification number 99, acetyl ester number 228 (corresponding with 75.6% of thujyl alcohol). No thujone could be detected (*Jaarboek Dept. Landb. Ned. Ind.*, 1906, 44). *Lantana odorata*, from Jamaica, gave 0.16% of lemon-yellow oil, having an odour of hyssop and ambergris, and having  $D^{15}$  0.9149,  $[\alpha]_D - 1^\circ 36'$ ,  $n_D^{20}$  1.49630, ester number 4.7, acetyl ester number 51.0. *Tugetea patula*, flowers, from Mexico, yielded 0.1% of a golden-yellow oil, having  $D^{15}$  0.8856,  $[\alpha]_D - 5^\circ 35'$ ,  $n_D^{20}$  1.49714, acid number 2.0, ester number 18.7, acetyl ester number 74.3.

The report concludes with a critical résumé of descriptions of essential oils in various pharmacopeias, notes on recent chemical, biological, and physical research work on terpenes and their derivatives, and a memoir on the history, botany, preparation, and composition of Japanese peppermint oil by N. Inouye. T. A. H.

**Oxidation Products of Artemisin.** ENRICO RIMINI (*Atti R. Accad. Lincei*, 1908, [v], 17, ii, 590—597).—The arteminic acid described by Horst (Abstr., 1902, i, 387) as an oxidation product of artemisin is in reality a mixture of santonin and artemisin, its formation being due to the use of impure artemisin.

When artemisin is oxidised by alkaline permanganate (about 5 atoms of oxygen) in presence of ice, it yields a *ketonic acid*,  $C_{15}H_{22}O_8$ , in the form of a pale yellow syrup, which reduces ammoniacal silver nitrate solution and Fehling's solution in the cold, and yields iodoform with potassium hydroxide and iodine. The *diphenylhydrazone* of this acid,  $C_{15}H_{22}O_8(N_2HPh)_2$ , forms chrome-yellow crystals, m. p. 116—118° (decomp.).

If a large excess of permanganate is employed, the oxidation of artemisin (1 mol.) yields oxalic acid (1 mol.). T. H. P.

**Rhein.** OTTO A. OESTERLE and ED. TISZA (*Chem. Zentr.*, 1908, ii, 1929—1930; from *Schweiz. Woch. Chem. Pharm.*, 1908, 46, 701—703. Compare Hesse, Abstr., 1900, i, 41).—When crystallised about twenty times from pyridine, and sublimed in a cathode ray vacuum, this substance was obtained in small, yellow needles or compact, dark-coloured crystals, m. p. 321—321.5°, which gave on analysis 63.98, 63.71% C, and 2.88, 2.81% H, corresponding with  $C_{15}H_8O_8$ , the formula suggested by Tschirch and Heuberger (Abstr., 1903, i, 108). When acetylated in pyridine solution, no higher acetyl derivative was obtained than the diacetate. When heated with propionic anhydride, a pyridine solution of rhein yields a lemon-yellow, crystalline *propionate*, m. p. 223—224°; analysis gave 68.21% C, and 4.43% H. Benzoylation of rhein appears to result in the formation of at least two products, which have not yet been separated.

Methylation with methyl sulphate gives several *methyl ethers*, of which one, insoluble in hot potassium hydroxide, crystallises in long, pale yellow needles, m. p. 288°. The conclusion is drawn that rhein is not a simple substance, but a mixture. J. V. E.

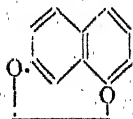
**The Green Pigment of Bile.** MAURICE PIETTRE (*Compt. rend.*, 1908, 147, 1492—1495).—Bilirubin crystallises from benzyl chloride in long prisms, often arranged in bundles; it crystallises still better from a mixture of chloroform and carbon tetrachloride. The formation of biliverdin is not simply an oxidation, for a green coloration is also produced when the halogens, the halogen acids in glacial acetic acid, trichloroacetic acid, chloral, bromal, etc., act on bilirubin.

G. B.

**Establishment of the Oxonium Theory.** HERMAN DECKER and THEODOR VON FELLENBERG (*Annalen*, 1909, 364, 1—44).—The salts of benzopyryonium, naphthapyryonium, and dibenzopyryonium, can only be regarded as compounds containing quadrivalent oxygen, and the authors consider that the existence of quadrivalent basic oxygen is thereby established on as firm a basis as that of quinquivalent nitrogen, quadrivalent sulphur, and trivalent iodine. The compounds regarded by Collie and Tickle, Bæyer and Villiger, Hewitt and Werner, Fosse, etc., as oxonium salts, in spite of doubts which have been expressed as to this formulation, are correctly so constituted, and this also applies to Kehrman's azoxonium compounds. The authors are in entire agreement with the views of Archibald and McIntosh (*Trans.*, 1904, 85, 919) on this subject, and they discuss at length the general resemblance between oxonium and ammonium compounds. It is pointed out that the secondary valencies of oxygen are usually brought into play at a lower temperature than in the case of nitrogen; thus oxonium compounds often decompose, or even cannot exist, at a temperature at which ammonium compounds are quite stable. In this respect quadrivalent sulphur occupies a position intermediate between nitrogen and oxygen. The formation of alkylammonium salts, as in the expression:  $\text{HI} + \text{NH}_2\text{Me} \rightleftharpoons \text{NH}_3\text{MeI} \rightleftharpoons \text{NH}_3 + \text{MeI}$ , whereby the quaternary compound may decompose in two directions (to which phenomenon the term "heterospasis" is applied), has its counterpart in the case of oxygen compounds, and the formation of oxonium intermediate compounds, with their possibility of heterospasis, in many cases throws light on hitherto incompletely explained reactions.

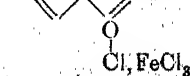
The synthesis of benzopyryonium derivatives is effected conveniently by condensing salicylaldehyde and its derivatives in presence of sulphuric or hydrochloric acid with an aliphatic or aromatic aldehyde or ketone containing an acidic methylene group next to the carbinol group. Solutions of such pyryonium salts in 10–15% hydrochloric acid are mostly yellow, and on dilution, or by partial neutralisation, become colourless and deposit the corresponding colourless carbinol. Benzopyryonium ferrichloride is best prepared by shaking salicylaldehyde (2 mols.) and acetaldehyde (1 mol.) with 70% sulphuric acid and warming the mixture for three-quarters of an hour on the water-bath. After precipitating tar with hydrochloric acid, solid ferric chloride, is added. In moist air it becomes black, loses hydrogen chloride, and coumarin is formed. 2-Methylbenzopyryonium salts (*Abstr.*, 1907, i, 1064) are similarly prepared by the condensation of salicylaldehyde and acetone. The condensation of methyl ethyl ketone and salicylaldehyde in presence of sodium hydroxide leads to the formation of *o*-hydroxystyryl ethyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COEt}$ , in small, yellow crystals, m. p.  $101^\circ$  (corr.), and a small amount of a compound,  $\text{C}_{22}\text{H}_{22}\text{O}_3$ , in yellow leaflets, m. p.  $246\text{--}247^\circ$  (corr.). The former, on warming with fuming hydrochloric acid and adding ferric chloride, yields 2-ethylbenzopyryonium ferrichloride,  $\text{C}_{11}\text{H}_{11}\text{OCl}\cdot\text{FeCl}_3$ , in flesh-coloured crusts, m. p.  $68\text{--}70^\circ$  (corr.), after sintering at  $65^\circ$ . The salt becomes green on exposure to light, and decomposes under the influence of moisture. When salicylaldehyde and methyl ethyl

ketone are subjected to the action of hydrogen chloride and ferric chloride added to the purified product, 2:3-dimethylbenzopyronium ferrichloride,  $C_{11}H_{11}OCl, FeCl_3$ , is formed in long, yellow needles, m. p. 117—118° (corr.), after sintering at 112°. On dissolving this in acetone and pouring into water, the base, probably dimethylbenzopyranol, is precipitated. 2-isoPropylbenzopyronium ferrichloride,  $C_{12}H_{13}OCl, FeCl_3$ , prepared by condensing salicylaldehyde and valer-aldehyde in presence of hydrogen chloride, and subsequently adding ferric chloride, forms long, yellow needles, m. p. 75·5—76·5° (corr.). 3-Methyl-2-ethylbenzopyronium ferrichloride,  $C_{12}H_{13}OCl, FeCl_3$ , similarly prepared from salicylaldehyde and diethyl ketone, forms golden leaflets, m. p. 86·5—87·5° (corr.). With water it yields 3-methyl-2-ethylbenzopyranol,  $C_{12}H_{14}O_2$ , in small, colourless needles, m. p. 70—72° (corr.). The condensation of salicylaldehyde and dipropyl ketone results in the production of a compound,  $C_{21}H_{26}O_2$ , colourless, glistening leaflets, m. p. 106—107° (corr.), and, on adding ferric chloride to the filtrate from this, 3-ethyl-2-propylbenzopyronium ferrichloride,  $C_{14}H_{17}OCl, FeCl_3$ , in yellow, glistening leaflets, m. p. 55°, which with water gives 3-ethyl-2-propylbenzopyranol, in colourless needles, m. p. 74—76°. 2-Phenylbenzopyronium ferrichloride is obtained in a 70% yield by condensing salicylaldehyde and acetophenone. 2:3-Diphenylbenzopyronium ferrichloride,  $C_{21}H_{15}OCl, FeCl_3$ , similarly obtained from salicylaldehyde and deoxybenzoin, crystallises in long, yellow needles, m. p. 123—124° (corr.). With water this yields 2:3-diphenylbenzopyranol,  $C_{21}H_{16}O_2$ , in colourless needles, m. p. 121—122° (corr.). On boiling this with methyl or ethyl alcohol, the corresponding ether is formed. 7-Hydroxy-2-phenylbenzopyronium chloride has the formula  $C_{15}H_{15}O_4Cl$  (Perkin, Robinson, and Turner, Trans., 1898, 93, 1098, give  $C_{15}H_{13}O_3Cl$ ). On heating at 140° in a current of hydrogen chloride the compound,  $C_{15}H_{11}O_2Cl$ , is formed. The picrate of the base turns brown at 190° and begins to sinter; it is not completely melted at 270° (Bülow and Sicherer, Abstr., 1902, i, 113, give m. p. 232—233°). The ferrichloride forms small, yellow needles containing  $1C_2H_4O_2$  (from acetic acid), m. p. 162—163° (corr.), after previous sintering.



As a consequence of their work on benzopyronium salts, the authors consider that salts of phenacetein, resacetatein, gallacetein, quinacetein, isobrasilein, isohama-tein, fluorescein, and coerulein are to be looked on as benzopyronium salts, and suggest that the free bases contain the annexed chromogen.

2-Phenyl-naphthapyronium ferrichloride (annexed formula), prepared by condensing  $\beta$ -naphthaldehyde and acetophenone and precipitating with ferric chloride, forms small, dark yellow needles, m. p. 187·5° (corr.). On pouring into water, the colourless carbinol separates. 2:3-Diphenyl-naphthapyronium ferrichloride,



$C_{25}H_{17}OCl, FeCl_3$ , similarly prepared from  $\beta$ -naphthaldehyde and deoxybenzoin, crystallises in small, slender, yellow needles, m. p. 205—206° (corr.); the carbinol base forms two picrates, that

with two mols. of picric acid forms dark-coloured crystals, m. p. 118—120°, and that with 1 mol. of picric acid gives smaller crystals, m. p. 161° (decomp.), after sintering at 145°. J. C. C.

**Cheiroline, the Alkaloid containing Sulphur obtained from Wallflower Seeds.** WILHELM SCHNEIDER (*Ber.*, 1908, 41, 4466—4470).—The formula assigned by Wagner to cheiroline (*Abstr.*, 1908, i, 202) is incorrect; it should be  $C_9H_{16}O_5N_2S_2$ . Cheiroline is practically a neutral substance, and is optically inactive; it gives a white precipitate with mercuric chloride, and when warmed with an alkaline solution of lead oxide yields lead sulphide, and with an ammoniacal silver solution forms a mirror and silver sulphide. When the solution obtained by boiling the alkaloid (1 mol.) with dilute aqueous sodium hydroxide is acidified, it evolves hydrogen sulphide (1 mol.) and carbon dioxide (about 1.4 mols.). The solution then contains a base,  $C_8H_{11}O_2NS$ , which is obtained as an exceedingly deliquescent, crystalline mass; the *hydrochloride*,  $C_8H_{11}O_2NS \cdot HCl$ , crystallises in almost colourless, deliquescent, prismatic needles, m. p. 145—146°. The base when treated with sodium ethoxide and methyl iodide yields a quaternary *methiodide*,  $C_8H_{18}O_2NIS$ , obtained as glistening, silky scales, m. p. 183°; it is therefore probable that the base is a primary base.

Since cheiroline readily parts with a carbon atom and a sulphur atom, yielding a strong base, it is probable that these atoms are connected to the two nitrogen atoms as in thiocarbamide.

W. H. G.

**Ergot of Rye.** ERNST VAHLEN (*Archiv exp. Path. Pharm.*, 1908, 60, 42—75).—The author controverts the statement of Barger and Dale (*Abstr.*, 1908, i, 204) that the crystalline product, clavin, previously isolated from ergot, is a mixture of leucine and tartaric acid. He shows that by means of cupric acetate or hydroxide it can be resolved into two constituents, one of which gives an insoluble copper salt, whereas the other gives a soluble salt. The latter is a weakly basic substance of the formula  $C_6H_{11}O_2N$ , m. p. 258—260°, and does not give precipitates with the ordinary alkaloidal reagents; the former is *L*-leucine. For these reasons, the formula  $C_{11}H_{24}O_4N_2$  is assigned to clavin. Clavin, leucine, and the clavin base are all very similar to one another in their crystalline form, solubility in solvents, and capacity for subliming, and the clavin is regarded as the leucine salt of the base.

The author also criticises Dale's experiment on the physiological action, and maintains, in opposition to Dale, that clavin has a specific action on the uterus.

Experiments were also carried out to determine the physiological action of the alkaloids, ergotinine, and hydroergotinine, which were isolated and described by Kraft. The latter has been assumed to be identical with the so-called ergotoxine, the water-soluble, amorphous alkaloid isolated by Barger and Carr (*Trans.*, 1907, 91, 337). It was found that more than 16 decigrams per kilo. was the toxic dose of hydroergotinine for cats, whereas, according to Dale (*Abstr.*, 1907, i, 79), 1.5 mg. of ergotoxine phosphate was a toxic dose for the same

animals. For these reasons, the chemical identity of hydroergotine and ergotoxine cannot be regarded as proved. It is suggested that both might be contaminated with varying quantities of a highly toxic substance. Ergotinine is relatively non-toxic when compared with hydroergotinine.

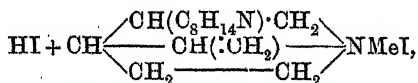
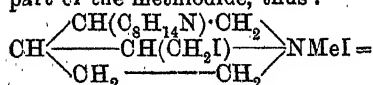
An experiment was made with the crystalline secalaminosulphonic acid, which was isolated by Kraft. It was found, when injected into a frog, to be physiologically inert. It is not, therefore, the active principle in the preparations described as sclerotic and ergotic acids.

S. B. S.

*apoMorphine Hydrochloride.* DAVID B. DOTT (*Pharm. J.*, 1908, [iv], 27, 801).—Experiments have been made which indicate that *apomorphine hydrochloride* has the composition represented by the formula  $C_{34}H_{30}O_5N_2 \cdot 2HCl \cdot 2H_2O$ , in which it is assumed that *apo-morphine* is formed by the condensation of 2 mols. of morphine with elimination of 1 mol. of water.

E. G.

**Action of Acids on Di-iodo- $\alpha$ -methylsparteine.** AMAND VALEUR (*Compt. rend.*, 1908, 147, 1318—1319. Compare Abstr., 1908, i, 1006).—When *iodoisosparteine methiodide* is heated with either dilute sulphuric, hydrochloric, or acetic acid and the solution cooled, the product is invariably *iodoisosparteine methiodide hydriodide*,  $C_{15}H_{25}N_2MeI_2 \cdot HI$ , m. p.  $198^\circ$ , which regenerates *iodoisosparteine methiodide* when treated with sodium carbonate. The reaction is probably to be explained by the separation of hydrogen iodide from part of the methiodide, thus:



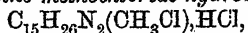
and the subsequent action of the liberated hydrogen iodide on the unchanged methiodide. This view is supported by the fact that the mother liquors from the action of dilute acetic acid on the methiodide contain a small quantity of a substance containing approximately the proportion of iodine required by the above formula. Moreover, when *iodoisosparteine methiodide* is heated in a sealed tube with dilute sodium hydroxide solution at  $125$ — $130^\circ$ ,  $\alpha$ -methylsparteine is formed, probably according to the reaction  $C_{15}H_{25}N_2MeI_2 + 2NaOH = C_{15}H_{25}N_2Me + 2NaI + O + H_2O$ , the oxygen liberated serving to oxidise part of the  $\alpha$ -methylsparteine produced.

E. H.

**Relation between  $\alpha$ -Methylsparteine and *isoSparteine*. Reciprocal Transformation of these Bases. II. *isoSparteine-methosulphate* and Some Salts of this Base. III. Action of Alkalis on *isoSparteinemethosulphate*. Methyl*isoSparteinium* Hydroxide.** AMAND VALEUR (*Bull. Soc. chim.*, 1909, [iv], 5, 31—37, 37—40, 40—42).—The first paper is theoretical, and gives an interpretation of results recorded in the second and third papers and other

work (Abstr., 1908, i, 1006) on the basis of the formulæ previously assigned to sparteine,  $\alpha$ -methylsparteine, and *isosparteine* (Abstr., 1905, i, 659, 717; 1908, i, 206). Most of this work has been published already (*loc. cit.*, and 1908, i, 736).

*isoSparteine methosulphate* (*loc. cit.*) dissolves in 1.5 parts of water, and the solution is slightly bitter, neutral to litmus, and does not reduce potassium permanganate. The anhydrous salt has m. p. 140—140.5°. *isoSparteine methochloride hydrochloride*,



m. p. 192—193° (decomp.),  $[\alpha]_D - 19.75^\circ$ , obtained by adding barium chloride to the solution of the methosulphate, separates from alcohol on addition of acetone, in transparent, deliquescent crystals. *isoSparteine methobromide hydrobromide*, m. p. 193° (decomp.),  $[\alpha]_D - 15.38^\circ$ , similarly obtained, is crystalline and very soluble in water. Its solution, on addition of sodium hydroxide, deposits an oil, which soon crystallises, and is probably *isosparteine methobromide*. *isoSparteine methiodide hydriodide* (Abstr., 1908, i, 44) has  $[\alpha]_D - 11.80^\circ$ , and crystallises from alcohol with  $1\text{H}_2\text{O}$ .

*Sparteine methosulphate*,  $\text{C}_{15}\text{H}_{26}\text{N}_2\text{Me}\cdot\text{HSO}_4\cdot 7\text{H}_2\text{O}$ ,  $[\alpha]_D - 24.54^\circ$ , obtained by the addition of the necessary quantity of sulphuric acid to  $\alpha$ -methylsparteinium hydroxide, crystallises from water on addition of alcohol and acetone. The solution is slightly acid to litmus, and does not reduce permanganate.

The transformation of *isosparteine* into  $\alpha$ -methylsparteine described previously (Abstr., 1908, i, 736) may be used for the recovery of  $\alpha$ -methylsparteine from the mixture of bases obtained in methylating sparteine (Abstr., 1908, i, 44). The mixture is treated with sulphuric acid, whereby the  $\alpha$ -methylsparteine is converted into *isosparteine methosulphate*, the other bases remaining unchanged. The latter are washed out with ether, and the residual methosulphate converted into  $\alpha$ -methyl*isosparteinium* hydroxide by the action of baryta, and this into  $\alpha$ -methylsparteine.

T. A. H.

**Strychnos Alkaloids. II. New Method for the Preparation of Sulphonic Acids.** HERMANN LEUCHS and WILHELM SCHNEIDER (*Ber.*, 1908, 41, 4393—4396. Compare Abstr., 1908, i, 563).—It is extremely difficult to obtain strychninesulphonic acids by the direct action of sulphuric acid on the alkaloid, but *strychninesulphonic acid*,  $\text{C}_{21}\text{H}_{22}\text{O}_5\text{N}_2\text{S}$ , is readily formed when sulphur dioxide is passed into warm water (60°) in which finely-divided strychnine and manganese dioxide are suspended. The acid crystallises from hot water in colourless needles containing water of crystallisation, which is given up at 105°. The dried acid is extremely hygroscopic, and has m. p. 350—360° (decomp.). It dissolves readily in dilute alkalis, but not in 20% hydrochloric acid. The solution in sodium hydroxide has  $[\alpha]_D^{20} - 233^\circ$ . A hot solution of the sodium salt deposits the free acid when cooled.

J. J. S.

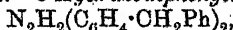
**Aqueous Solutions of Pyridine.** ÉMILE BAUD (*Compt. rend.*, 1909, 148, 96—98).—From determinations of the electro-capillary maxima of mixtures of water and pyridine, Gouy (Abstr., 1906, ii, 725) deduced the existence of a compound of these substances. To

the same end the author has studied the freezing temperatures, contractions in volume, refractive indices, and heats of dissolution of similar mixtures. The curve obtained by plotting the solidification temperatures of mixtures of pyridine and water against their percentage composition consists sensibly of four straight lines: the first, extending from 0 to 55% of pyridine, representing the separation of ice; the second, from 55 to 77% of pyridine, that of a hydrate; the third, from 77 to 83% of pyridine, of another hydrate, whilst the fourth represents the separation of pure pyridine. The temperature reaches a minimum for 83% of pyridine ( $C_5H_5N + 0.9H_2O$ ), which is accordingly the composition of a eutectic mixture. As the crystallisation curves of the hydrates intersect before the maximum, the composition of these hydrates cannot be deduced; all that can be concluded is that one contains more than  $3.6H_2O$  and the other more than  $1.3H_2O$  per molecule of pyridine. The curve drawn with percentages of pyridine by weight as abscissæ, and the contractions in volume of these mixtures as ordinates, exhibits a maximum for the mixture of the composition  $C_5H_5N, 2H_2O$ . The index of refraction curve has a maximum also at the mixture of this composition. The heat of dissolution of pure pyridine in a large excess of water diminishes with rise in temperature according to the expression  $Q = 2.800 - 0.044(t - 12.5)$ . Determination of the heats of dissolution of the mixtures of water and pyridine permits of the calculation of the heats of formation of the latter. By calculating the results with reference to the addition of increasing quantities of water to a molecule of pyridine, a smooth curve is obtained exhibiting a change of direction at  $2H_2O$  and  $6H_2O$ , whilst calculation of the heats for the same volume of mixture gives a curve showing a maximum for  $C_5H_5N, 2H_2O$ .

The conclusion is drawn that aqueous pyridine solutions contain at least two hydrates,  $C_5H_5N, 2H_2O$  and  $C_5H_5N, 6H_2O$ , dissociated at the ordinary temperature, the more complex being the more dissociated.

E. H.

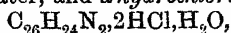
**Alkaline Reduction of *o*-Nitrodiphenylmethane.** PAUL CARRE (*Compt. rend.*, 1909, 148, 101—103\*).—When *o*-nitrodiphenylmethane (Geigy and Königs, *Abstr.*, 1885, 1236) is reduced by gradually adding zinc dust to its boiling solution in alcoholic soda, only 15—20% of *o*-hydrazodiphenylmethane is formed, the main product being *o*-aminodiphenylmethane. *o*-Hydrazodiphenylmethane,



crystallises in white lamellæ, m. p. 148—149°. It is oxidised by mercuric oxide to *o*-azodiphenylmethane,  $N_2(C_6H_4 \cdot CH_2Ph)_2$ , which exists in two forms. The  $\alpha$ -modification crystallises from acetic acid in red needles, m. p. 116—117°, which, on melting, are transformed into the  $\beta$ -modification, m. p. 124—125°. The latter, when recrystallised from acetic acid, regenerates the  $\alpha$ -compound, whilst crystallisation of either from alcohol gives a mixture of the two forms. When *o*-hydrazodiphenylmethane is treated with dilute acids, it undergoes the benzidine transformation, giving 2:2'-dibenzyl-4:4'-diaminodiphenyl,  $C_{12}H_8(CH_2Ph)_2(NH_2)_2$ , which crystallises in long, white

\* and *Bull. Soc. chim.*, 1909, [iv], 5, 119—121.

needles, m. p.  $136^{\circ}$ , and forms a *sulphate*,  $C_{26}H_{24}N_2 \cdot H_2SO_4$ , also crystallising in long, white needles, m. p.  $255^{\circ}$  (decomp.), rapidly dissociated by boiling water, and a *hydrochloride*,



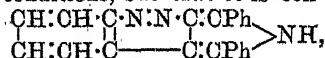
crystallising in white needles, m. p.  $214^{\circ}$  (decomp.), hydrolysed by water.

*o*-Aminodiphenylmethane,  $NH_2 \cdot C_6H_4 \cdot CH_2Ph$ , prepared by Fischer and Schutte (Abstr., 1894, i, 200), but not obtained by them in a crystalline form, crystallises from ether in large, light yellow prisms, m. p.  $52^{\circ}$ , b. p.  $190-191^{\circ}/22$  mm.,  $172-173^{\circ}/12$  mm. Its *hydrochloride*,  $C_{18}H_{18}N \cdot HCl$ , crystallises in white needles, m. p.  $137^{\circ}$  (decomp.), which are dissociated by boiling water. The amine, when heated with phenylthiocarbimide, gives  $\alpha$ -phenyl- $\beta$ -*o*-diphenylmethane-thiocarbamide,  $NHPh \cdot CS \cdot NH \cdot C_6H_4 \cdot CH_2Ph$ , a white, crystalline powder, m. p.  $138^{\circ}$ .  
E. H.

**Reaction of Phenylhydrazine and  $\alpha$ -Halogen Aryl Derivatives.** GUIDO GOLDSCHMIEDT (*Gazzetta*, 1908, 38, ii, 634-638).—The results obtained by Ponzio and Valente (Abstr., 1908, i, 458) had been published previously by Ofner (Abstr., 1904, i, 818) and Flaschner (Abstr., 1905, i, 936).  
T. H. P.

**Transformations of Diazopyrroles.** FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1908, [x], 17, ii, 655-662).—Castellana and D'Angelo (Abstr., 1905, i, 646) found that prolonged boiling of diazophenylindole with dilute sulphuric acid converts it into the corresponding azo-derivative.

The author finds that diazotriphenylpyrrole does not undergo a similar transformation under the same conditions, but that it is converted into an isomeric compound,



which acts both as an acid and as a base, dissolves readily in alcoholic potassium hydroxide solution, giving a violet solution, and separates in cinnabar-red scales; with strong acids it gives insoluble blue salts. When treated with ethyl iodide in presence of sodium ethoxide, it is converted into the *ethyl* derivative,  $C_{22}H_{14}N_2 \cdot Et$ , which crystallises from alcohol in shining, indigo-blue needles, m. p.  $181^{\circ}$ . By the action of nitric acid on an acetic acid solution of the compound,  $C_{22}H_{15}N_3$ , the

latter is converted into a *diketone*,  

$$\begin{array}{c} CH:CH \cdot C \cdot N=N \\ CH:CH \cdot C \cdot CBz:CBz \end{array}$$
 which separates

from alcohol in brownish-yellow crystals, m. p.  $163^{\circ}$ , dissolves in concentrated sulphuric acid, giving a blue solution, and is converted by hydrazine into the corresponding *azine*,  $C_{22}H_{14}N_4$ , crystallising from alcohol in golden-yellow needles, m. p.  $240^{\circ}$ , and subliming undecomposed.

Reduction of the diketone by means of zinc dust and acetic acid yields the compound,  

$$\begin{array}{c} CH:CH \cdot C \cdot N:N \cdot C:CPh \\ CH:CH \cdot C \text{---} C:CPh \end{array} > O,$$
 which crystallises from acetic acid in shining, red needles, m. p.  $195^{\circ}$ , and is oxidised to the diketone by the action of nitric acid.  
T. H. P.

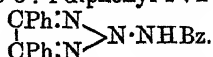
**Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXV. *N*-Amino-osotriazoles.** ROBERT STOLLÉ (*J. pr. Chem.*, 1908, [ii], 78, 544—546. Compare Abstr., 1907, i, 654).—The author now draws the conclusion that the compound obtained by the complete hydrolysis of 2:3-dibenzoyl-5:6-diphenyl-2:3-dihydro-1:2:3:4-tetrazine, which was thought previously to be 5:6-diphenyl-2:3-dihydro-1:2:3:4-tetrazine (Abstr., 1905, i, 97),

is 1-amino-3:4-diphenyl-1:2:5-triazole,  $\begin{smallmatrix} \text{CPh:N} \\ \text{CPh:N} \end{smallmatrix} > \text{N} \cdot \text{NH}_2$ , since when

it is benzoylated it yields a compound isomeric with the dibenzoyl derivative just mentioned, but having m. p. 151°; this compound is

1-dibenzoylamino-3:4-diphenyl-1:2:5-triazole,  $\begin{smallmatrix} \text{CPh:N} \\ \text{CPh:N} \end{smallmatrix} > \text{N} \cdot \text{NBz}_2$ . It

is also formed when 2:3-dibenzoyl-5:6-diphenyl-2:3-dihydro-1:2:3:4-tetrazine is heated at about 190°, and by the benzoylation of the compound obtained by eliminating one of the benzoyl groups from the above dibenzoyltetrazine; the latter compound must be therefore 1-benzoylamino-3:4-diphenyl-1:2:5-triazole,



It has also been shown that 2:3-dibenzoyl-5:6-dimethyl-2:3-dihydro-1:2:3:4-tetrazine when heated at about 150° passes into

1-dibenzoylamino-3:4-dimethyl-1:2:5-triazole,  $\begin{smallmatrix} \text{CMe:N} \\ \text{CMe:N} \end{smallmatrix} > \text{N} \cdot \text{NBz}_2$ , m. p. 114°. W. H. G.

**Addition of Hydrogen Chloride to Organic Bases and Azo-compounds.** ANTONI KORCZYŃSKI (*Ber.*, 1908, 41, 4379—4381. Compare Abstr., 1908, i, 977; Scholl and Escalles, *ibid.*, 1898, i, 182).—The absorption of hydrogen chloride by organic amines and azo-derivatives has been examined at various temperatures, and in an apparatus similar to that used by Ley and Wiegner. The maximum number of molecules of hydrogen chloride absorbed is not a function of the strength of the base. At -75° aniline, *p*-toluidine, and *o*- and *m*-nitroanilines form salts with 3HCl, and dibromo-*p*-toluidine and *p*-nitroaniline with 2HCl. At the ordinary temperature, azobenzene, *p*-hydroxyazobenzene, *p*-methoxyazobenzene and aminoazobenzene absorb 2HCl, and dimethylaminoazobenzene, 3HCl. J. J. S.

**The Combination of Iodine in Iodothyreoglobulin, and some Observations on Iodothyryn.** ADOLF OSWALD (*Arch. exp. Path. Pharm.*, 1908, 60, 115—130).—The degradation of iodothyreoglobulin by pancreatin and barium hydroxide solution was studied. By means of the former, a small amount of a substance was obtained, which deposited from the digest, and was soluble in alkalis, but insoluble in acids; it contained 3—4.5% iodine, and was in many respects similar to Baumann's iodothyryn; the greater part of the iodine found in the digest was not in combination with organic substances. By scission with barium hydroxide, also, only a small

amount of an organic iodine compound was obtained, which was soluble in acids, and was probably unchanged thyreoglobulin.

S. B. S.

**The Mono-amino-acids of Paramucin.** FRITZ PREGL (*Zeitsch. physiol. Chem.*, 1908, 58, 229—232).—After acid hydrolysis, paramucin yields glucosamine, diamino-acids in traces, leucine, alanine, proline, phenyl-alanine, aspartic acid, glutamic acid, tyrosine, and tryptophan. Quantitative data are not given. W. D. H.

**Hydrolysis of Glutokyryin.** MAX SIEGFRIED and O. PILZ (*Zeitsch. physiol. Chem.*, 1908, 58, 215—228).—Glutokyryin  $\beta$ -sulphate was prepared from gelatin; the phosphotungstic acid precipitate from it contains 80% of its nitrogen. Arginine, lysine, and glutamic acid were found in the cleavage products after hydrolysis. Histidine and glycine were not obtained. W. D. H.

**Molecular Analysis of Proteins.** ALEXANDRE ÉTARD and ANTONY VILA (*Compt. rend.*, 1908, 147, 1323—1324. Compare Abstr., 1908, i, 584).—The use of anhydrous methyl alcohol is advocated for separating and drying the mixtures of amino-acids formed in protein hydrolysis. A solution of barium hydroxide in anhydrous methyl alcohol is employed for precipitating the acidic substances thus obtained. G. B.

**The Influence of Acids, Alkalis, Neutral Salts, and Carbohydrates on Trypsin.** T. KUDO (*Biochem. Zeitsch.*, 1909, 15, 473—500).—Tryptic digestion with "pancreatin Rhenania" proceeds best in a neutral medium. It is inhibited by alkalis and acids, especially organic acids. Sodium carbonate has a very small destructive influence on the ferment, acetic acid is indifferent, other organic acids destroy it, and mineral acids are rather more powerful in this direction. The destructive action is independent of their valency or concentration. Various salts have an inhibitory action, but in most cases a slight one. Starch is also inhibitory, but the sugars have little or no effect. W. D. H.

**The Adsorption of Diastase and Catalase by Colloidal Protein and by Normal Lead Phosphate.** AMOS W. PETERS (*J. Biol. Chem.*, 1908, 5, 367—380).—A method of concentration of enzymes is described, in which the enzyme is adsorbed from solution by the addition of lead phosphate suspended in water, or by peptone suspended in 50% acetone. Almost the whole of the enzyme is adsorbed, and remains active in spite of the presence of the adsorbed precipitate, from which it can only be separated to a slight extent by washing with water. The diastase employed was obtained from germinating wheat, from autolysed liver, and from liquid bacterial cultures. The action of diastase is accelerated by the presence of lead phosphate, but not, for instance, by that of zinc phosphate; the reason for the acceleration is unknown. G. B.

## Organic Chemistry.

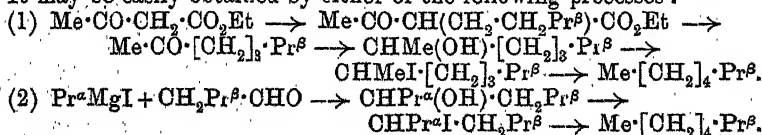
**Chemical Action of the Electric Discharge at Low Temperatures.** E. BRINER and E. L. DURAND (*J. Chim. Phys.*, 1909, 7, 1—30).—Most of the results described in this paper have been published already (Abstr., 1907, ii, 759; 1908, ii, 101, 940). By the action of the electric spark on a mixture of nitrogen and ethane at  $-78^{\circ}$ , carbon, hydrogen, nitric acid, ammonia, and higher hydrocarbons are obtained, the latter being formed by polymerisation. In similar experiments with a mixture of nitrogen and acetylene, similar products were obtained, but in the latter case the proportion of hydrogen cyanide predominates over that of the ammonia.

In the action of the silent discharge on ethane alone at  $-78^{\circ}$ , no carbon is liberated, but there is considerable formation of higher hydrocarbons. Under similar conditions, a mixture of equal volumes of nitrogen and ethane also gives a relatively high proportion of higher hydrocarbons, and less hydrogen cyanide than when the spark discharge is used.

The effect of the electric discharge is very complicated, and it appears that the laws of chemical statics are not applicable; kinetic and atomic considerations afford a better guide to the phenomena.

G. S.

**isoOctane [ $\beta$ -Methylheptane].** LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1909, 31, 107—116. Compare Abstr., 1907, i, 169).— $\beta$ -Methylheptane is the ninth hydrocarbon of the series  $C_8H_{18}$  to be prepared. It may be easily obtained by either of the following processes:



Methyl isohexyl ketone has b. p.  $165^{\circ}/764$  mm.; Welt gives b. p.  $167$ — $168^{\circ}$  (Abstr., 1895, i, 202). It is reduced by sodium and ethyl alcohol to methylisohexylcarbinol, b. p.  $176^{\circ}/765$  mm. (compare Welt, *loc. cit.*), and methylisohexylpinacolone,

$\text{Pr}^{\beta}\cdot[\text{CH}_2]_3\cdot\text{CMe}(\text{OH})\cdot\text{CMe}(\text{OH})\cdot[\text{CH}_2]_3\cdot\text{Pr}^{\beta}$ ,  
a liquid, b. p.  $293$ — $295^{\circ}/765$  mm. The latter compound is converted by hydrogen iodide into  $\eta$ -iodo- $\beta$ - $\zeta$ -tetramethyldodecan- $\zeta$ -ol,

$\text{Pr}^{\beta}\cdot[\text{CH}_2]_3\cdot\text{CMe}(\text{OH})\cdot\text{CMeI}\cdot[\text{CH}_2]_3\cdot\text{Pr}^{\beta}$ ,  
an unstable, colourless oil (compare Clarke and Shreve, Abstr., 1906, i, 473). Methylisohexylcarbinol is converted by red phosphorus and iodine into  $\zeta$ -iodo- $\beta$ -methylheptane, a colourless, heavy oil, which, when reduced with a zinc-copper couple, yields isooctane ( $\beta$ -methylheptane),  $\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{Pr}^{\beta}$ , a colourless liquid, b. p.  $116^{\circ}/761$  mm.,  $D_{25}^{20}$  0.7035,  $n_D^{25}$  1.3944. The reduction may also be effected by acting on the iodo-octane with magnesium in dry ether, and treating the organo-magnesium compound with water.

Propyl magnesium iodide and *isovaleraldehyde* interact in dry ether, forming an additive product, which, when treated with water, yields  *$\beta$ -methyl- $\delta$ -heptanol*,  $\text{CHPr}^a(\text{OH})\cdot\text{CH}_2\text{Pr}^b$ , a colourless liquid, b. p.  $164^\circ/760$  mm. If the reacting substances are not quite dry, *isoamyl alcohol* and a *glycol*,  $\text{CH}_2\text{Pr}^b\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Pr}^b$ , a colourless, viscid oil, b. p.  $238-242^\circ/760$  mm., are formed.  *$\beta$ -Methyl- $\delta$ -heptanol* is converted by red phosphorus and iodine into  *$\delta$ -iodo- $\beta$ -methylheptane*, which is reduced by a zinc-copper couple to  *$\beta$ -methylheptane*.

W. H. G.

**Production of Iodoform [from Carbon Dioxide].** GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1909, [vi], 29, 54-55).—Potassium hypochlorite added gradually to an aqueous solution containing ammonia, potassium hydroxide, 10% of potassium iodide, and 5% of potassium carbonate, forms nitrogen iodide, which at first disappears on shaking. When the disappearance becomes slow, a large excess of ammonia is added, which causes an almost immediate precipitation of iodoform.

G. B.

**Reactions between Iodoform and Silver Fluoride and Chloride.** WILLIAM OECHSNER DE CONINCK (*Bull. Soc. chim.*, 1909, [iv], 5, 62-63. Compare Auger, Abstr., 1908, i, 494).—On gently heating silver chloride and iodoform in the correct proportions suspended in dilute alcohol, the following interaction takes place:  $3\text{AgCl} + \text{CHI}_3 = 3\text{AgI} + \text{CHCl}_3$ . No gas is evolved, whereas if silver fluoride is taken (as Auger has shown) the products are carbon monoxide and hydrogen fluoride with a little carbon dioxide:  $3\text{AgF} + \text{CHI}_3 + \text{H}_2\text{O} = 3\text{AgI} + 3\text{HF} + \text{CO}$ .

R. J. C.

**Preparation of Absolute Alcohol.** M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. Chim. suc. dist.*, 1909, 26, 580).—Ninety to 95% alcohol is digested with aluminium foil in presence of mercuric chloride and then distilled. The product consists of absolute alcohol free from aldehydes and acetals.

L. DE K.

**Butane- $\beta$ -ol [Methylethylcarbinol] and its Tartrates.** J. RICHÉ (*J. Pharm. Chim.*, 1909, [vi], 29, 57-60).—This alcohol, synthesised from acetaldehyde by Grignard's reaction, could not be resolved into its optical antipodes by fractional esterification with tartaric acid.

G. B.

**Pinacolyl Alcohols.** MAURICE DELACRE (*Bull. Soc. chim.*, 1909, [iv], 5, 109-113).—The author questions the accuracy of the following conclusions given in L. Henry's recent papers on pinacolyl alcohols (Abstr., 1907, i, 374; 1908, i, 881; this vol., i, 79).—(1) That the haloid esters of *sec*-pinacolyl alcohol (methyl*tert*-butylcarbinol) undergo isomerisation when heated, yielding haloid esters of *tert*-pinacolyl alcohol (dimethylisopropylcarbinol); (2) that since on dehydration with acetic anhydride both pinacolyl alcohols yield a mixture of  $\beta\gamma$ -dimethyl- $\Delta^2$ -butylene and  $\beta\gamma$ -dimethyl- $\Delta^1$ -butylene, in which the former largely preponderates, it may be assumed

generally that the hydroxyl of a  $\text{:C(OH)\cdot}$  group placed near a  $\text{:OH\cdot}$  and a  $\text{\cdotCH}_2\text{\cdot}$  group exhibits a marked, but not exclusive, preference for the H of the  $\text{:CH\cdot}$  group, and (3) that in the dehydration of dimethylisopropylcarbinol by acetic anhydride containing sulphuric acid, the anhydride acts by first forming dimethylisopropylcarbinyl acetate, which is more readily dehydrated than the parent alcohol.

The author contends that the first statement is refuted by the results given in his previous papers (Abstr., 1907, i, 578; 1908, i, 243), and that the second conclusion is inadmissible since the relative proportions of the two hydrocarbons formed vary with the conditions of the experiment. The validity of the third point he has examined by treating dimethylisopropylcarbinyl acetate with dilute sulphuric acid, and finds that the acetate is scarcely dehydrated at all under conditions in which the alcohol undergoes complete dehydration (Abstr., 1906, i, 921).

T. A. H.

$\psi$ -Butylethylene Glycol. F. CLAESSENS (*Bull. Soc. chim.*, 1909, [iv], 5, 113—118).— $\psi$ -Butylethylene ( $\gamma$ -dimethyl- $\Delta^{\alpha}$ -butylene,  $\text{CMe}_3\text{\cdotCH\cdotCH}_2$ ),

described by Delacre (Abstr., 1902, i, 79), furnishes a liquid *dibromide*, b. p. 91—92°/14 mm. (approx.), 203°/762 mm. (decomp.),  $D^{20}$  1.616, which becomes coloured on keeping, is readily soluble in organic solvents, and when heated with potassium acetate and acetic acid in a closed tube at 200° is converted into *bromo- $\gamma$ -dimethyl- $\Delta^{\alpha}$ -butylene*, b. p. 120—130°,  $D^{20}$  1.165, which was not obtained pure.

On oxidation with permanganate,  $\gamma$ -dimethyl- $\Delta^{\alpha}$ -butylene yields trimethylacetic acid, and is therefore an exception to Wagner's rule that, on careful oxidation with permanganate, ethylenic hydrocarbons yield the corresponding glycols (Abstr., 1888, i, 665). With iodine and yellow mercuric oxide the hydrocarbon yields the corresponding *iodohydrin*,  $D^{14.81}$ , which decomposes at 110°, but is volatile in steam. On treatment with potassium hydroxide solution, this yields the corresponding *glycol*,  $\text{CMe}_3\text{\cdotCH(OH)\cdotCH}_2\text{\cdotOH}$ ,  $D^{50}$  0.940, b. p. 205—206°, m. p. 32—33°, which is crystalline and hygroscopic. The glycol dissolves in hydrochloric acid, from which it can be recovered unchanged. With acetyl chloride it yields, apart from a small quantity of a chlorinated compound, a *diacetyl* derivative, b. p. 213—215°,  $D^{20}$  1.014, which is a liquid of pleasant odour and readily soluble in water, alcohol or ether. Couturier's hydrocarbon,  $\beta$ - $\gamma$ -dimethyl- $\Delta^{\alpha}$ -butylene (Abstr., 1893, i, 244, and Delacre, Abstr., 1902, i, 79), can also be converted into the corresponding glycol through the iodohydrin. This glycol furnishes a chloroacetate on treatment with acetyl chloride, and dissolves in hydrochloric acid, yielding a chlorinated product which decomposes on distillation.

T. A. H.

New Method for Preparation of Ethers. JEAN B. SENDERENS (*Compt. rend.*, 1909, 148, 227—229).—The author has recorded previously the decomposition of alcohols into ethylenic hydrocarbons and water by the catalytic action of precipitated alumina at 300° (Abstr., 1908, i, 494, 495; ii, 166). It is now found that this substance at a lower temperature can effect the quantitative dehydration of

alcohols with production of the corresponding ethers. Thus alcohol in the state of vapour is passed over alumina (prepared by acidifying a solution of sodium aluminate) at 240–260°, and the products passed through a Y-tube cooled in ice. It is not necessary to use absolute alcohol. The products condense to a liquid which separates into two layers; the upper layer consists of ethyl ether in a state of greater purity than commercial "rectified ether." Methyl ether and propyl ether have been prepared in the same manner. W. O. W.

**Action of Acids on Sodium Ethyl Thiosulphate. III.** AUGUST GUTMANN (*Ber.*, 1909, 42, 228–232. Compare Abstr., 1907, i, 671; 1908, i, 497).—The action of alkalis on sodium ethyl thiosulphate is represented thus:  $\text{NaEtS}_2\text{O}_3 + \text{KOH} = \text{NaKSO}_3 + \text{EtSOH}$ . Bunte (*Ber.*, 1874, 646) represents the corresponding acid hydrolysis in the following manner:  $\text{NaEtS}_2\text{O}_3 + \text{H}_2\text{O} = \text{NaHSO}_4 + \text{EtSH}$ . The author finds that sulphurous acid is also produced whether the reaction is carried out in concentrated or dilute solution, or in presence of much or little acid. The other products are ethyl sulphide, sulphuric acid, and ethyl mercaptan. Probably the change in acid solution, as in alkaline, is at first:  $\text{HEtS}_2\text{O}_3 + \text{H}_2\text{O} = \text{SO}_2 + \text{H}_2\text{O} + \text{EtS}\cdot\text{OH}$ .

Subsequently in acid solution the sulphurous acid reacts with one or two molecules of thioethyl hydroperoxide, thus:  $\text{EtS}\cdot\text{OH} + \text{SO}_2 = \text{EtSH} + \text{SO}_3$ ;  $2\text{EtS}\cdot\text{OH} + \text{SO}_2 = \text{Et}_2\text{S}_2 + \text{H}_2\text{SO}_4$ .

That this explanation is correct is shown by the fact that if after alkaline hydrolysis a solution of sodium ethyl thiosulphate is rendered acid and kept, sulphuric acid is formed.

In view of these results, thiosulphuric acid can no longer be given the constitution  $\text{SO}_2\text{<}\begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$ , ascribed to it by Bunte, but it must exist as the two isomeric forms:  $\text{SO}_2\text{<}\begin{smallmatrix} \text{S}\cdot\text{OH} \\ \text{H} \end{smallmatrix}$  and  $\text{SO}_2\text{<}\begin{smallmatrix} \text{O}\cdot\text{SH} \\ \text{H} \end{smallmatrix}$ .

E. F. A.

**Acid Glycerophosphates.** P. CARRÉ (*Bull. Soc. chim.*, 1909, [iv], 5, 109).—With reference to a paper by Self (*Pharm. J.*, 1908, 26, 627), it is pointed out that the process described by that investigator for the preparation of barium hydrogen glyceryl phosphate, namely, the addition of sulphuric acid to barium glyceryl phosphate until the mixture is neutral to helianthin, has been shown by the present author on a previous occasion to yield a mixture of the normal glyceryl phosphate and glyceryl dihydrogen phosphate (Abstr., 1904, i, 133 215, 819).

T. A. H.

**The Nitrogen of Lecithin and other Phosphatides.** HUGH MACLEAN (*Biochem. J.*, 1909, 4, 38–58).—The nitrogen of the commercial preparation of lecithin termed "lecithol" (Riedel, Berlin) is probably all present as choline.

In the lecithin of heart-muscle there is probably another nitrogen-containing group in addition. The base of cuorin is probably not choline.

W. D. H.

**Allylxanthic Acid.** BERNARDO ODDO and GIOVANNI DEL ROSSO (*Gazzetta*, 1909, 39, i, 11—23).—Study of allylxanthic acid and of its salts and other derivatives shows that in some ways the xanthic acids are comparable with hydrogen sulphide and with cyanic and thiocyanic acids.

*Potassium*,  $\text{SK} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5$ , and *sodium allylxanthates*,  
 $\text{SNa} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5$ ,

obtained by the action of excess of carbon disulphide on a solution of potassium (or sodium) hydroxide in allyl alcohol at a low temperature, form white, gelatinous precipitates, which dry in the form of faintly yellow, silky needles. With copper sulphate these salts react according to the equations:  $2\text{SK} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5 + \text{CuSO}_4 = (\text{C}_3\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S})_2\text{Cu} + \text{K}_2\text{SO}_4$  and  $2(\text{C}_3\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S})_2\text{Cu} = (\text{C}_3\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S})_2\text{Cu}_2 + \text{C}_3\text{H}_5 \cdot \text{O} \cdot \text{CS} \cdot \text{S} \cdot \text{S} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5$

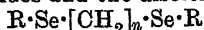
(compare Ragg, *Abstr.*, 1908, i, 604), the *cuprous allylxanthate* formed being insoluble. The allylxanthic radicle in the potassium and sodium salts may be estimated by titration with standard copper sulphate solution, using *s*-diphenylcarbazine as indicator (compare Oddo, *Abstr.*, 1903, ii, 758). The following salts of allylxanthic acid were also prepared: *silver*,  $\text{C}_4\text{H}_5\text{OS}_2\text{Ag}$ , *zinc*,  $(\text{C}_4\text{H}_5\text{OS}_2)_2\text{Zn}$ , *lead*,  $(\text{C}_4\text{H}_5\text{OS}_2)_2\text{Pb}$ , *nickel*,  $(\text{C}_4\text{H}_5\text{OS}_2)_2\text{Ni}$ , *cobalt*,  $(\text{C}_4\text{H}_5\text{OS}_2)_2\text{Co}$ , *mercury*, *cadmium*, *tin*, *bismuth*, *iron*, *platinum*, and *gold*.

*Allylxanthic acid*,  $\text{SH} \cdot \text{CS} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$ , is obtained as a faintly yellow, unstable oil heavier than water, and, on distillation, decomposes into allyl alcohol and carbon disulphide. The *methyl ester*,  $\text{SMe} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_3\text{H}_5$ , is a pale yellow oil, b. p. 200—203°,  $D_{25}^{25} 1.1214$ , with an alliaceous odour, and has the normal molecular weight in freezing benzene. The *ethyl ester*,  $\text{C}_6\text{H}_{10}\text{OS}_2$ , is an oil, b. p. 210—212°,  $D_{25}^{25} 1.0690$ , resembling the methyl derivative in odour, and having the normal molecular weight in freezing benzene. The *allyl ester*,  $\text{C}_7\text{H}_{10}\text{OS}_2$ , is obtained as a brownish-yellow oil, b. p. 221—223°, having a very pungent, garlic-like odour, and exhibiting normal cryoscopic behaviour in benzene.

T. H. P.

**Selenomercaptans and their Derivatives.** LEO TSCHUGAEFF (*Ber.*, 1909, 42, 49—54).—Ethyl, propyl, and butyl selenomercaptans have been prepared by heating on the water-bath a solution of sodium hydroselenide, obtained by saturating a 10% alcoholic solution of sodium ethoxide with hydrogen selenide with about 5% less than the calculated quantity of the alkyl iodide or bromide in an atmosphere of hydrogen. The selenomercaptans are heavy liquids with a foul, persistent odour, which are insoluble in water, react in the usual way with mercuric oxide, and yield coloured precipitates with the salts of heavy metals, particularly of lead and thallium. Selenomercaptans are extremely autoxidisable in air, yielding diselenides,  $\text{R} \cdot \text{Se}_2 \cdot \text{R}$ . The hydrogen of the  $\cdot\text{SeH}$  group reacts with magnesium methyl iodide, methane being evolved quantitatively. Selenides,  $\text{R}' \cdot \text{Se} \cdot \text{R}''$ , are obtained by treating an alcoholic solution of sodium ethoxide and the selenomercaptan with an alkyl iodide or bromide, all in equal molecular quantities; in the absence of air, the yield is nearly quantitative. Diselenides of the type  $\text{R} \cdot \text{Se} \cdot [\text{CH}_2]_n \cdot \text{Se} \cdot \text{R}$  result by the

action of dihaloid hydrocarbons on the sodium selenomercaptides:  $2\text{NaSeR} + \text{Br}[\text{CH}_2]_n\text{Br} = \text{R}\cdot\text{Se}[\text{CH}_2]_n\cdot\text{Se}\cdot\text{R} + 2\text{NaBr}$ . With ethylene dibromide, however, the main product is diethyl diselenide, ethylene being evolved. The selenides and the diselenides of the type



are colourless liquids somewhat stable in air, whilst diselenides of the type  $\text{R}\cdot\text{Se}_2\cdot\text{R}$  are yellowish-red liquids, which distil undecomposed only in a vacuum.

In the accompanying table, the density, refractive index, and coefficient of expansion ( $\alpha$ ) are measured at the temperature  $t^\circ$ .

	B. p.	$t^\circ$ .	$D_4^{25}$	$\alpha$ .	$n_D^{25}$
EtSeH .....	53.5°	24	1.3954	0.0018	1.47715
PrSeH .....	84	20	1.3020	—	1.47560
BuSeH .....	114	24.5	1.2352	0.0012	1.47446
MeSeEt .....	86	23	1.3134	—	1.4820
MeSePr .....	114	20.4	1.2445	—	1.48121
MeSeBu .....	141	24.5	1.1875	—	1.47710
PrSePr .....	159	24.3	1.1427	0.00113	1.47494
PrSe <sub>2</sub> ·Pr .....	99/13 mm.	22.2	1.4991	0.00127	1.55535
EtSe $[\text{CH}_2]_2$ ·SeEt .....	135/15 mm.	24	1.4630	0.00129	1.54892

The atomic refraction of selenium in the selenomercaptans is 10.78, in the selenides, 10.91, and in dipropyldiselenide, 11.33. C. S.

**Solidification of Mixtures of Water and Soluble Fatty Acids.** A. FAUCON (*Compt. rend.*, 1909, 148, 38—39).—The freezing-point curves of the systems water-formic acid, water-acetic acid, and water-propionic acid have been determined. The respective eutectic points and the molar composition of the eutectic mixtures are as follows:  $\text{H}\cdot\text{CO}_2\text{H} + 1.14\text{H}_2\text{O}$ ,  $-48^\circ$ ;  $\text{Me}\cdot\text{CO}_2\text{H} + 2.40\text{H}_2\text{O}$ ,  $-27^\circ$ ;  $\text{Et}\cdot\text{CO}_2\text{H} + 0.578\text{H}_2\text{O}$ ,  $-29.4^\circ$ . In no case is there evidence of chemical combination. The system butyric acid and water is being further investigated. G. S.

**Behaviour of Fatty Acids in Arnold's Distillation Process.** A. HEIDUSCHKA and K. PFIZENMAIER (*Pharm. Zentr.-h.*, 1909, 50, 85—86).—With reference to the publications of Dons (*Zeitsch. Nahr. Genussm.*, 1907, 14, 150) and Arnold (*ibid.*, 1908, 16, 705) on the subject of the fatty acids of butter, the author has investigated the behaviour of each of the acids, formic, acetic, propionic, butyric, hexoic, octoic, deoic, lauric, myristic, palmitic, stearic, oleic, and linoleic, when mixed with water and distilled. It was found that (1) the distillate may have a constant composition which has no relation to the composition of the mixture under distillation, or (2) its composition may vary with that of the mixture under distillation, or (3) it may exhibit a combination of (1) and (2), being of constant composition for a certain concentration of the mixture under distillation and exhibiting a proportional composition for other concentrations. A table of experimental results is given in the original. T. A. H.

**Total Asymmetric Syntheses.** ALFRED BYK (*Ber.*, 1909, 42, 141—142).—Mainly a criticism of Henle and Haack's paper (this vol., i, 6). J. J. S.

**General Method for the Preparation of Trialkylacetic Acids.** ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 148, 127—132. Compare Abstr., 1908, i, 987; this vol., i, 108).—Trialkylacetophenones of the type  $\text{COPh}\cdot\text{CRR}'\text{R}''$  are dissolved in benzene or toluene and boiled for five hours with sodamide. The ketone undergoes decomposition into benzene and an amide of the type  $\text{CRR}'\text{R}''\cdot\text{CO}\cdot\text{NH}_2$ , which is readily converted by nitrosyl sulphate into the corresponding acid,  $\text{CRR}'\text{R}''\cdot\text{CO}_2\text{H}$ . Attempts to bring about a similar reaction in the case of dialkylallylacetophenones, however, have not been successful. The following new compounds have been prepared in this way: *aa*-dimethyl-*n*-butyramide,  $\text{CMe}_2\text{Et}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 103—104°; *aa*-dimethyl-*n*-valeramide,  $\text{CMe}_2\text{Pr}^a\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 95—96°; *aa*-dimethyl-*n*-valeric acid,  $\text{CMe}_2\text{Pr}^a\cdot\text{CO}_2\text{H}$ , b. p. 101—102°/11 mm., 190—200° under ordinary pressure; *a*-methyl-*a*-ethyl-*n*-butyramide,  $\text{CMeEt}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 78—79°; *aa*-diethyl-*n*-butyramide,  $\text{CEt}_2\cdot\text{CONH}_2$ , m. p. 108°, b. p. 148—149°/30 mm.; *aa*-diethyl-*n*-butyric acid,  $\text{CEt}_2\cdot\text{CO}_2\text{H}$ , m. p. 39.5°, b. p. 119°/14 mm., 220—222° under ordinary pressure; *a*-methyl-*a*-ethyl-*n*-valeramide,  $\text{CMeEtPr}^a\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 46°, b. p. 134—135°/12 mm.; *a*-methyl-*a*-ethyl-*n*-valeric acid,  $\text{CMeEtPr}^a\cdot\text{CO}_2\text{H}$ , b. p. 215—220°. W. O. W.

**Further Applications of the General Method of Hydrogenation Based on the Use of Finely-divided Metals.** PAUL SABATIER and ALPHONSE MAILHE (*Ann. Chim. Phys.*, 1909, [viii], 16, 70—107).—Mainly a résumé of work already published (compare Abstr., 1905, i, 571, 635; 1906, i, 561; 1907, i, 458, 488, 490, 587, 747; 1908, i, 36, 278, 529), but the following facts have not previously been recorded: (1) unsaturated acids of the aliphatic series yield the corresponding saturated acid when directly hydrogenated in the presence of nickel; thus crotonic acid at 190° is reduced to butyric acid, and oleic or elaidic acid at 280—300° is reduced to stearic acid to the extent of 90% of that required by theory; (2) unsaturated ketones are converted into the corresponding saturated ketone by direct hydrogenation in the presence of nickel; thus mesityl oxide yields isopropylacetone ( $\beta$ -methylpentan-3-one), and phorone yields diisobutyl ketone; (3) when the ketonic acids are directly hydrogenated in the presence of nickel, the ketonic group only is reduced; thus levulic acid yields valerolactone, and ethyl acetoacetate undergoes (a) the normal reduction, yielding ethyl butyrate; (b) scission of the molecule and subsequent reduction of the products, yielding acetone, isopropyl alcohol, and propionic acid; and (c) a molecular condensation yielding solid dehydracetic acid.

Methyl *tert*-butylamine has b. p. 54—56°, and the oxalate has m. p. 166° (not 58—60° and 160° respectively as stated previously: Abstr., 1907, i, 490). M. A. W.

**Action of Ozone on Oleic Acid.** CARL D. HARRIES [with WALTHER FRANK] (*Ber.*, 1909, 42, 446—458. Compare Molinari, Abstr., 1908, i, 849, and Harries, *ibid.*, 387).—Oleic acid ozonide,

after washing with sodium hydrogen carbonate solution and water, has the same composition whatever the concentration of the ozone used may be.

The formation of hydrogen peroxide by the decomposition of the ozonide with water is confirmed. The decomposition with water yields products containing 9, and not 18, carbon atoms, and the primary products are aldehydes or their peroxides, which are transformed into acids by a secondary reaction. These products have been re-investigated (compare Abstr., 1907, i, 10). Nonaldehyde peroxide,  $C_9H_{16}O_8$ , crystallises from light petroleum in glistening plates, m. p.  $73^\circ$ , and has all the characteristic properties of a peroxide. Its b. p. under reduced pressure is higher than that of nonaldehyde, but lower than that of pelargonic acid. When boiled with water it yields nonaldehyde and hydrogen peroxide. The other products isolated were pelargonic acid and the semi-aldehyde of azelaic acid, all of which are obtained from the original ethereal extract. The aqueous solution, when acidified, yields an ethereal extract from which the peroxide of the semi-aldehyde of azelaic acid,  $C_9H_{16}O_4$ , and azelaic acid have been isolated. The peroxide crystallises from acetone in needles, m. p.  $98^\circ$ , and is completely soluble in hot water, but is partly converted into the semi-aldehyde and hydrogen peroxide and partly isomerised to azelaic acid. J. J. S.

**Semi-aldehyde of Succinic Acid [ $\beta$ -Aldehydopropionic Acid].**—CARL D. HARRIES and ERNST ALEFELD (*Ber.*, 1909, 42, 159—165. Compare Harries, Abstr., 1898, i, 232).— $\beta$ -Aldehydopropionic acid has been described by Perkin and Sprankling as a thick, dark yellow oil which is readily oxidised by atmospheric oxygen to succinic acid (*Trans.*, 1899, 75, 11). von Ungern-Sternberg prepared  $\beta$ -aldehydopropionic acid from aconic acid, and describes it as an oil solidifying to a white, crystalline mass, m. p.  $147^\circ$ , b. p.  $234$ — $236^\circ/760$  mm., which is very stable towards oxidising agents, but nevertheless has the properties of an aldehydo-acid; thus it yields a phenylhydrazone-phenylhydrazone, m. p.  $182^\circ$ . The conclusion drawn by this author was that Perkin and Sprankling were either not working with  $\beta$ -aldehydopropionic acid, or else that their statement as to the readiness with which the acid underwent oxidation was incorrect (*Diss.*, Königsberg, 1904).

The present authors have prepared  $\beta$ -aldehydopropionic acid by decomposing allylacetic acid ozonide with water. They obtained it as an oil which was readily oxidised by atmospheric oxygen, forming succinic acid. The oil when kept for a few days, however, solidified to a white, crystalline mass, m. p.  $147^\circ$ , identical with the substance described by von Ungern-Sternberg. Mol.-wt. determinations show that the oily acid is unimolecular, whereas the solid acid is bimolecular (compare following abstract).

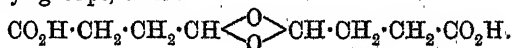
*Allylacetic acid ozonide*,  $O_3 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$ , prepared by the action of ozone on a solution of allylacetic acid in carbon tetrachloride, is a colourless syrup,  $D_{20}^{25}$  1.289,  $D_{20}^{25}$  1.297,  $n_D^{25}$  1.46552,  $n_D^{25}$  1.47359; it is decomposed by water, yielding formic acid, form-

aldehyde, succinic acid, and  $\beta$ -aldehydopropionic acid; it is probable that the peroxide of the latter substance is formed at the same time.

The unimolecular  $\beta$ -aldehydopropionic acid is a colourless, viscid liquid, b. p. 134—136°/14 mm.,  $D_{25}^{25}$  1.2568,  $n_D^{25}$  1.44873,  $n_D^{25}$  1.44571,  $n_D^{25}$  1.45911; it follows from these physical constants, and from the absence of a ferric chloride reaction, that the substance is the aldehyde form of the acid. The *semicarbazone*,

$\text{NH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{N} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , crystallises in small prisms or needles, m. p. 177—178° (decomp.); the *p*-nitrophenylhydrazone,  $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_3$ , forms golden-yellow leaflets, m. p. 158°. W. H. G.

**$\beta$ -Aldehydopropionic Acid.** CARL D. HARRIES and ALFRED HIMMELMANN (*Ber.*, 1909, 42, 166—167).—The crystalline  $\beta$ -aldehydopropionic acid, prepared from allylacetic acid (compare preceding abstract) or from aconic acid (compare von Ungern-Sternberg, *Diss.*, Königsberg, 1904), is shown to have the bimolecular formula  $(\text{C}_4\text{H}_2\text{O}_3)_2$ . It yields the unimolecular variety when distilled at 134—136° under a pressure of 14 mm. The stability of the polymerised form towards oxidising agents shows that the condensation occurs between the two carbonyl groups, thus:



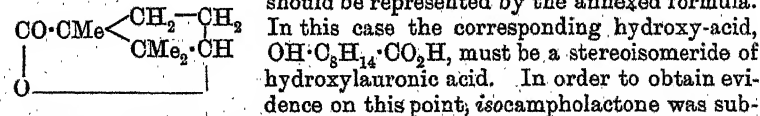
W. H. G.

**Molecular Rearrangements in the Camphor Series. I. Hydroxylauronic Acid and *iso*Campholactone.** WILLIAM A. NOYES and A. W. HOMBERGER (*J. Amer. Chem. Soc.*, 1909, 31, 278—281).—It has been shown (Abstr., 1895, i, 295) that aminolauronic acid is converted by nitrous acid into  $\gamma$ -lauronic acid, laurolene, and *isocampholactone*.

When ethyl aminolauronate is treated with nitrous acid, it yields a mixture of ethyl  $\gamma$ -lauronolate and ethyl hydroxylauronate. *Ethyl  $\gamma$ -lauronolate*,  $\text{C}_8\text{H}_{13} \cdot \text{CO}_2\text{Et}$ , b. p. 110—115°/25 mm., has  $D_4^{20}$  0.9514 and  $[\alpha]_D^{25} + 56.6^\circ$ . *Ethyl hydroxylauronate*,  $\text{OH} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{Et}$ , b. p. 150°/30 mm., has  $D_4^{20}$  1.100 and  $[\alpha]_D^{25} + 6.73^\circ$ .

Evidence is given to show that hydroxylauronic acid has the formula  $\text{CO}_2\text{H} \cdot \text{CMe} \begin{array}{c} \diagup \text{CH}_2 - \text{CH}_2 \\ \diagdown \text{CMe}_2 \cdot \text{CH} \cdot \text{OH} \end{array}$ , which is supported by the fact that the acid is oxidised by nitric acid to active camphoronic acid.

The method of formation of *isocampholactone* suggests that it should be represented by the annexed formula.

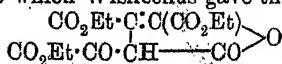


*lactone*,  $\text{C}_8\text{H}_{12}\text{O}_4$ , an acid, m. p. 228°, probably camphononic acid, and a compound, m. p. 111°, which is probably a lactone. The *lactone*,  $\text{C}_8\text{H}_{12}\text{O}_4$ , m. p. 122°, b. p. 272°, is the chief product of the oxidation, and crystallises in needles. These results do not justify any conclusion with regard to the structure of *isocampholactone*. E. G.

**Ethyl Nitrososuccinate.** JULIUS SCHMIDT and KARL TH. WIDMANN (*Ber.*, 1909, 42, 497—501).—A general method for the production of nitroso-compounds is to pass the nitrous gases from the action of nitric acid on arsenious oxide into acylcarboxylic esters. The method gives especially good results when the acyl group is attached to a tertiary carbon atom.

Ethyl acetylsuccinate when treated with the gas at 0° in a long, narrow tube, then, after two hours, evacuated in a dark glass desiccator, forms *ethyl nitrososuccinate*,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{NO})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , an azure-blue liquid which cannot be distilled and is decomposed quickly by light. It is, however, pure; in a ethylene dibromide solution it is unimolecular (found 185 and 194, calc. 203),  $D_4^{18} 1.20$ ,  $n_D^{18} 1.4419$ . The compound gives Liebermann's reaction, is stable in ethylene dibromide, but in alcohol or ether the cold solution is slowly decolorised, quickly when warm. This change may be due either to polymerisation or isomeric change to oximino-compounds. Potassium permanganate, Caro's acid, or hydrogen peroxide (10%) oxidise it to *ethyl nitrosuccinate*,  $\text{C}_8\text{H}_{13}\text{O}_6\text{N}$ , a yellow, viscous oil, which could not be distilled unchanged under diminished pressure, and explodes when quickly heated. On reduction with zinc dust and acetic acid, ethyl aspartate is formed, b. p. 126—127°/10 mm., 150—152°/25 mm. (compare Fischer, *Abstr.*, 1901, i, 193); the *picrolonate*,  $\text{C}_8\text{H}_{13}\text{O}_4\text{N}$ ,  $\text{C}_{10}\text{H}_{15}\text{O}_5\text{N}$ , forms yellow crystals, m. p. 290°. W. R.

**Products of Hydrolysis of Ethyl Dioxalylsuccinate.** *iso*Pyromucic Acid. EDMOND E. BLAISE and HENRI GAULT (*Compt. rend.*, 1909, 148, 176—179. Compare *Abstr.*, 1908, i, 713).—The authors consider that their experiments on the production of *iso*-pyromucic acid by the removal of  $\text{CO}_2$  from the product of hydrolysis of ethyl oxalylsuccinate furnish evidence against the constitutions ascribed by Wislicenus to the substances this author obtained by the action of alkalis on the ester (*Abstr.*, 1895, i, 506). Thus the compound to which Wislicenus gave the formula



should be represented as a  $\delta$ -lactone,  $\text{CO}_2\text{Et}\cdot\text{C}=\text{C}(\text{CO}_2\text{Et}) \begin{array}{c} \diagup \text{O} \\ \diagdown \text{CO}_2\text{Et}\cdot\text{C}(\text{OH})\cdot\text{CO} \end{array}$ ; the substance obtained from this by hydrolysis would then have the formula  $\text{CO}_2\text{H}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$ , which agrees more closely with the properties of the compound than the ketonic structure put forward by Wislicenus. W. O. W.

**Lævulinaldehyde.** CARL D. HARRIES and MAX BOEGEMANN (*Ber.*, 1909, 42, 439—446. Compare *Abstr.*, 1905, i, 364; 1906, i, 833).—The aldehyde was prepared by the action of water on methylheptenone ozonide (*Abstr.*, 1906, i, 226). It dissolves readily in water, and reduces cold Fehling's solution. Its molecular weight, as determined by the cryoscopic method in benzene solution, proves it to be unimolecular, and its molecular dispersion agrees with the ketoaldehydic constitution. Its dielectric constant, as determined by Nernst's

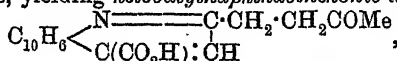
method, is high, namely, 32 at 18°, whereas the constant for succinaldehyde is 28.5 at 20°.

The dioxime has m. p. 76°; the *disemicarbazone*,  $C_7H_{14}O_2N_6$ , crystallises from methyl alcohol in colourless plates or prisms, m. p. 178—180°.

The diphenylhydrazone has not been obtained; phenylhydrazine reacts with an acetic acid solution of the aldehyde yielding an oil, which with hydrochloric acid forms phenylmethyldihydropyridazine. As this compound is sparingly soluble, it can be made use of in estimating the aldehyde.

The *di-p-nitrophenylhydrazone*,  $C_{17}H_{18}O_4N_6$ , crystallises in brown plates, m. p. 106°.

The aldehyde reacts with an alcoholic solution of pyruvic acid and  $\beta$ -naphthylamine, yielding *ketobutylnaphthacinchonic acid*,



which is sparingly soluble in all ordinary solvents.

Lævulinaldehyde differs from succinaldehyde, which also contains carbonyl groups in the  $\alpha\delta$ -positions, in the following points: (1) it does not polymerise; (2) it does not give Angeli's reaction with benzsulph-hydroxamic acid (Abstr., 1904, ii, 330), and (3) it is not readily converted into acetals by Laisen's method.

When reduced with a large excess of aluminium amalgam and ether, it yields  $\gamma$ -amylene glycol and Lipp's methyldihydrofuran (Abstr., 1889, 843).

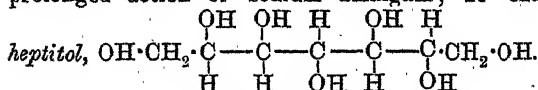
J. J. S.

**Certain Numerical Relations in the Sugar Group.**  
C. S. HUDSON (*J. Amer. Chem. Soc.*, 1909, 31, 66—86).—On the assumption that the known  $\alpha$ - and  $\beta$ -forms of dextrose and the related mutarotating sugars are the partial stereoisomerides indicated by the lactonic formula of Tollens, it is shown: (1) that the difference between the molecular rotations of the  $\alpha$ - and  $\beta$ -forms of all the aldehyde sugars, and all their derivatives in which the added substance is not joined directly to the end asymmetric carbon atom, is a nearly constant quantity; (2) that the  $\alpha$ - and  $\beta$ -forms of those derivatives of any aldose sugar in which only the end carbon atom is affected (*e.g.*, glucosides) have molecular rotations the sum of which is equal to the sum for the  $\alpha$ - and  $\beta$ -forms of the aldose, and it is shown from the available data that these deductions are valid. On this basis, the following rules are proposed for the naming of the  $\alpha$ - and  $\beta$ -forms of the sugars: The names are to be so selected that for all sugars which are genetically related to *d*-glucose the subtraction of the rotation of the  $\beta$ -form from that of the  $\alpha$ -form gives a positive difference, and for all sugars genetically related to *l*-glucose a negative difference. When the end carbon atom is affected, the above rule is modified as follows: The names of the  $\alpha$ - and  $\beta$ -forms are to be so selected that the difference of their molecular rotations is equal to, and of the same sign as, the similar difference for the forms of the similar derivative of that glucose (*d* or *l*) to which the first sugar is genetically related.

The equilibrium constant for the reversible reaction between the  $\alpha$ - and  $\beta$ -forms of the aldohexoses and allied disaccharides is approximately constant and equal to 1.5, a rule which permits of the calculation of the rotation of the unknown forms of certain sugars. From measurements of the "thermal lag" (compare Abstr., 1908, ii, 665), it is shown that in all cases the  $\alpha$ -form of the sugar is favoured by an increase in temperature.

A formula is deduced which allows of the calculation of the rotatory power of the unknown forms of many of the natural and synthetic glucosides. The influence of the end groups of the glucosides on the rotation of the carbon atom to which they are attached depends mainly on the weight of the group. G. S.

**Preparation and Properties of  $\beta$ -Glucoheptitol.** L. H. PHILIPPE (*Compt. rend.*, 1908, 147, 1481—1483).—The author has submitted Fischer's  $\beta$ -glucoheptose (Abstr., 1892, 1164) to the prolonged action of sodium amalgam; he thus obtains  $\beta$ -gluco-



This compound forms small, rectangular tablets, m. p. 130—131° on the Maquenne block;  $[\alpha]_D^{20} + 48'$  in aqueous solution. Its rotatory power serves to distinguish it from the isomeric  $\alpha$ -glucoheptitol (*loc. cit.*). Acetic anhydride in presence of zinc chloride converts it into a resinous *hepta-acetyl* derivative,  $\text{C}_7\text{H}_9(\text{OAc})_7$ , m. p. about 50°;  $[\alpha]_D^{20} + 34.8^\circ$ . The *heptabenzoyl* derivative,  $\text{C}_7\text{H}_9(\text{OBz})_7$ , forms prismatic needles, m. p. 182°. The *tribenzylidene* derivative,  $\text{C}_7\text{H}_{10}\text{O}_7(\text{C}_7\text{H}_5)_3$ , crystallises in very slender needles, m. p. about 230°. A *formalacetal* derivative has also been prepared. W. O. W.

**Hydrolysis of Maltose by Citric Acid.** JOSEPH PIERAERTS (*Bull. Assoc. Chim. suc. dist.*, 1909, 26, 562—573).—Hydrated maltose may be converted completely into 2 mols. of dextrose by boiling 50 c.c. of a 2½% solution with 10 c.c. of 20% citric acid for about thirty hours in a reflux apparatus. The time may be reduced to two hours and a-half by heating at a pressure of 1½ atm. As soon as the maltose is converted into dextrose, the liquid assumes a yellow colour, which darkens on prolonged heating. L. DE K.

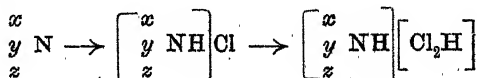
**Formation of Hydrocelluloses by means of Sulphuric Acid.** CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1909, 22, 155—156. Compare Büttner and Neuman (this vol., i, 86).—The author claims that elementary analyses are not sufficiently accurate to serve for the clear diagnosis of different hydrocelluloses. The reducing powers are much more accurate criteria. Both acids and alkalis hydrolyse hydrocelluloses. J. J. S.

**Acid Haloid Salts.** FELIX KAUFLE and E. KUNZ (*Ber.*, 1909, 42, 385—392. Compare Scholl and Escales, Abstr., 1898, i, 182; Korczyński, this vol., i, 123).—It is shown that a large number of

mono-amines combine with dry hydrogen chloride or bromide at the ordinary temperature, forming dihydrochlorides and dihydrobromides. The stability of the dihydrochloride depends largely on the degree of alkylation; thus tertiary and quaternary bases regularly form dihydrochlorides, whilst of the secondary bases only dimethylamine forms a dihydrochloride. Dihydrochlorides of methylamine, methyl-aniline, aniline, acetanilide, methyl-*o*-toluidine, diphenylamine, and tribenzylamine could not be obtained at the ordinary temperature.

When a compound contains several nitrogen atoms, it is found that each nitrogen atom reacts independently.

The conclusion is drawn that the compounds are in all cases ammonium salts of perhalogen hydrides. This is supported by the fact that the change of *p*-nitrosodimethylaniline hydrochloride into the dihydrochloride is not accompanied by a change of colour, as in the formation of the former from the base itself. The following formulation :



shows that in the conversion of the hydrochloride into the dihydrochloride, only the colourless anion undergoes alteration, whilst the ammonium part of the molecule, which imparts the colour to the substance, remains unchanged.

The following salts were prepared by passing the dry halogen hydride over the base or its normal haloid salt. They are all hygroscopic substances, and readily part with hydrogen chloride or bromide. *Dimethylamine dihydrochloride* is a white, crystalline substance. *Tetramethylammonium chloride hydrochloride*,  $\text{NMe}_4\text{Cl} \cdot \text{HCl}$ , forms a white, crystalline mass. *m-Nitrodimethylaniline dihydrochloride*,  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2 \cdot 2\text{HCl}$ , is a yellowish-white, crystalline mass. *p-Nitrosodimethylaniline dihydrochloride* is a yellow powder. *Dimethyl-*o*-toluidine dihydrochloride* was obtained as an oily liquid. *Diethylaniline dihydrochloride*,  $\text{C}_{10}\text{H}_{15}\text{N} \cdot 2\text{HCl}$ , forms colourless crystals, which solidify at  $47^\circ$ . *p-Nitrosodiethylaniline dihydrochloride* is a yellow powder. *Pyridine dihydrochloride*,  $\text{C}_5\text{H}_5\text{N} \cdot 2\text{HCl}$ , forms large, white prisms, m. p.  $46\text{--}7^\circ$ . *Quinoline dihydrochloride*,  $\text{C}_8\text{H}_7\text{N} \cdot 2\text{HCl}$ , is a crystalline mass having the same freezing point as the pyridine compound. *Tetramethyldiaminodiphenylmethane tetrahydrochloride*,  $\text{C}_{17}\text{H}_{22}\text{N}_2 \cdot 4\text{HCl}$ , is a brown solid. *Tetramethyldiaminodiphenyl ketone tetrahydrochloride* is obtained only at  $0^\circ$ . *p-Azotoluene dihydrochloride*,  $\text{C}_{11}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$ , is a chocolate-brown solid. *Diethylaminoazobenzene dihydrochloride* has the same red colour as the mono-hydrochloride. *Diethylaminoazobenzene- $\beta$ -naphthalene pentahydrochloride* resembles potassium permanganate in colour.

*Pyridine dihydrobromide*,  $\text{C}_5\text{H}_5\text{N} \cdot 2\text{HBr}$ , *quinoline dihydrobromide*, and *diethylaminoazobenzene pentahydrobromide* were also prepared.

W. H. G.

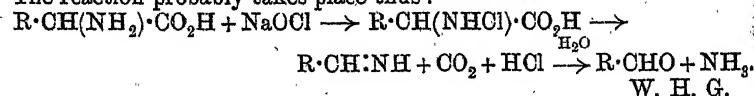
*d*-Propylenediamine and Derivatives of the Optically Active Propylenediamines. LEO TSCHUGAEFF and W. SOKOLOFF (*Ber.*, 1909, 42, 55—58. Compare *Abstr.*, 1907, i, 896).—The data

previously given for *l*-propylenediamine are to be corrected to  $D_4^{25}$  0.8612 and  $[\alpha]_D - 29.65^\circ$ .

*Cobalt-tri-l-propylenediamine iodide*,  $[\text{CoPn}_3]\text{I}_3$ , prepared in a similar manner to the racemic iodide (Pfeiffer and Gassmann, Abstr., 1906, ii, 614), separates from hot water in brownish-yellow needles containing  $2\text{H}_2\text{O}$ , is much more soluble than the racemic iodide, and for a sample dried at  $100^\circ$  shows  $[\alpha]_D + 23.63^\circ$  for  $p$  3.38 and  $D_4^{25}$  1.0156.

*d*-Propylenediamine, separated from the racemic base or from the non-crystallisable syrup remaining after the preparation of the *l*-isomeride (*loc. cit.*) by means of the *d*-propylenediamine hydrogen *l*-tartrate, has b. p.  $120.5^\circ$ ,  $D_4^{25}$  0.8584, and  $[\alpha]_D + 29.78^\circ$ , and yields, like the *l*-isomeride (*loc. cit.*), a *platinum di-d-propylenediamine chloride*,  $[\text{PtPn}_2]\text{Cl}_2$ , which has  $[\alpha]_D - 46.45^\circ$  for  $p$  8.27 and  $D_4^{25}$  1.0445, from which the *nitrate*,  $[\text{PtPn}_2](\text{NO}_3)_2$ , is obtained, having  $[\alpha]_D - 40.55^\circ$  for  $p$  8.36 and  $D_4^{25}$  1.0465. C. S.

**Degradation of  $\alpha$ -Amino-acids to Aliphatic Aldehydes by means of Sodium Hypochlorite.** KURT LANGHELD (*Ber.*, 1909, 42, 392—393).—Raschig has shown (Abstr., 1908, ii, 30) that chloramine is formed by the interaction of sodium hypochlorite and ammonia. A similar reaction appears to take place between sodium hypochlorite and  $\alpha$ -amino-acids; an intermediate product is formed, which does not colour aqueous aniline, and decomposes when the solution is warmed at  $40$ – $50^\circ$ , yielding ammonia, carbon dioxide, and an aliphatic aldehyde containing one carbon atom less than the acid. The reaction probably takes place thus:



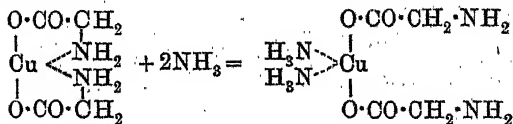
**Internally Complex Salts.** HEINRICH LEY (*Ber.*, 1909, 42, 354—376).—In the internally complex copper salts of  $\alpha$ -amino-acids the union of the metal to oxygen by a principal, and to nitrogen by a supplementary, valency linking (Abstr., 1905, i, 175) causes the properties, especially the colour and the dissociation, of these complex salts to differ from those of ordinary salts.

The electrolytic and the hydrolytic dissociation of copper glycine and of copper  $\alpha$ -alanine are very small; the solutions can be boiled without deposition of copper hydroxide. Such stability is not shown by the copper salts of all  $\alpha$ -amino-acids, those of piperidinoacetic or diethylaminoacetic acid (of the type  $\text{NR}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ) being slightly electrolytically, but considerably hydrolytically, dissociated; a complex nickel piperidinoacetate cannot be prepared by reason of its great hydrolytic dissociation. The complex copper salts of  $\beta$ -amino-acids are moderately hydrolytically dissociated, and in dilute solutions precipitation of copper hydroxide occurs. Complex copper salts of  $\delta$ -amino-acids, the formation of which would require the production of a seven-membered ring,  $\text{CH}_2\langle\text{CH}_2\cdot\text{CO}\cdot\text{O}\rangle\text{Cu}$ , cannot be obtained (compare Tschugaeff, Abstr., 1907, i, 392).

The fact that glycine can displace the metal from salts of stronger

$(\text{NH}_2 \cdot \text{R} \cdot \text{CO}_2)_2\text{M} + 2\text{HX}$ , where  $\text{M} = \text{Cu}, \text{Ni}, \text{Co}$ , or  $\text{Zn}$ , proceeding almost entirely from left to right in consequence of the very slight electrolytic dissociation of the complex salt. (The equation only partly represents what occurs; in addition, the acid  $\text{HX}$  forms a salt with the amino-acid. Since the salt formation is very small with acetic acid, the author uses acetates in the following experiments.) Conductivity measurements give some idea of what is happening in the reaction. The difference  $\Delta$  between the conductivities of the metallic acetate before and after the addition of the amino-acid is approximately a measure of the complex salt formation, because if  $(\text{NH}_2 \cdot \text{R} \cdot \text{CO}_2)_2\text{M}$  is largely formed, the conductivity of the solution will approach that of acetic acid, whilst the conductivity will be mainly due to the metallic acetate if complex salt formation is only small. In this way it is shown that barium, manganese, and cadmium have little tendency to form complex salts, and copper and nickel have a great tendency; the tendencies of cobalt and zinc are about the same, and much smaller than that of nickel. With nickel acetate and different amino-acids, the formation of internally complex salts decreases from glycine through  $\alpha$ - and  $\beta$ -aminopropionic acids to piperidinoacetic acid; with copper acetate and  $\gamma$ -aminobutyric acid, negative values of  $\Delta$ , that is, an increase of the conductivity, are observed, which is explained by the fact that a partial formation of basic copper acetate occurs in consequence of the large basic  $k$  value of the amphoteric electrolyte.

The abnormal colour of complex salts has been examined spectrometrically. The complex copper salts of glycine,  $\beta$ -aminopropionic acid, methylglycine, benzylglycine,  $\alpha\alpha$ -dimethylglycine,  $\alpha$ -phenylglycine, diethylglycine, and piperidinoacetic acid are all blue in the solid state and violet-blue in solution. The substitution of methylene hydrogen by phenyl does not produce any essential colour change. The replacement of aminic hydrogen by an aromatic group causes a great change in the absorption, internally complex copper anilinoacetate and its homologues being intensely green in the solid and the dissolved states. The addition of ammonium hydroxide to copper anilinoacetate causes a colour change from green to blue, probably by reason of the conversion of the internally complex salt into an ordinary complex salt; a similar conversion occurs with ammonium hydroxide and copper glycine, although here no essential colour change is observed:



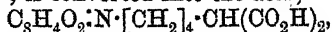
The decomposition of metallic acetates by amino-acids is accompanied by colour change when internally complex salts are formed; nickel acetate becomes distinctly blue by the addition of glycine or  $\alpha$ - or  $\beta$ -aminopropionic acid. It is noteworthy that the colour of cobalt acetate is unchanged by the addition of glycine, and also that solid cobalt anilinoacetate has the normal red colour.

It is well known that the strengths of amino-acids are increased by

the introduction of acyl groups. The metallic salts of aceturic acid (acetyl glycine) are strongly dissociated, and do not behave as internally complex salts, copper aceturate and nickel aceturate having the normal blue and green colours respectively. The ultraviolet absorption spectra of aqueous copper acetate in the presence of increasing amounts of ammonia indicate that  $\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2$  and  $\text{Cu}(\text{NH}_3)_4(\text{C}_2\text{H}_3\text{O}_2)_2$  respectively are present according as the concentration of the ammonia is small or large, thus confirming the results of the partition experiments previously described (*loc. cit.*).

The paper concludes with some remarks on the migration of cations of type  $\text{CO}_2\text{H}\cdot\text{R}\cdot\text{NH}_3$ . C. S.

**Some Derivatives of  $\delta$ -Aminocaproic [Hexoic] Acid.** AUGUST ALBERT (*Ber.*, 1909, 42, 556—558).—Ethyl  $\delta$ -phthaliminobutylmalonate (Abstr., 1899, i, 595), which crystallises from petroleum in needles, m. p.  $46^\circ$ , is converted into the acid,

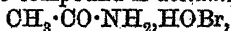


by warming for a short time with hydriodic acid; it crystallises from a mixture of ethyl acetate and benzene in needles, m. p.  $127^\circ$ , decomposing into  $\epsilon$ -phthaliminohexoic acid (Abstr., 1908, i, 649). As the yield of the latter was only 16%, another method for its preparation was devised.  $\epsilon$ -Chlorohexonitriles is obtained in 32% yield by heating pentamethylene chloride and potassium cyanide in aqueous alcohol solution for seven hours (compare von Braun and Steindorff, Abstr., 1905, i, 206). The portion b. p.  $242$ — $250^\circ$ , when heated with potassium phthalimide at  $210^\circ$ , is converted into crude  $\epsilon$ -phthaliminohexonitrile. This oil, when heated with double its volume of sulphuric acid for ten minutes at  $100^\circ$ , yields a mixture of  $\epsilon$ -phthaliminohexoamide,  $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_5\cdot\text{CO}\cdot\text{NH}_2$ , which crystallises from alcohol in leaflets, m. p.  $158^\circ$ , and the corresponding acid. The yield from the pentamethylene chloride is 12%.

Red phosphorus and bromine convert phthaliminohexoic acid into  $\alpha$ -bromo- $\epsilon$ -phthaliminohexoic acid,  $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_4\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ , which forms crystals, m. p.  $153$ — $153.5^\circ$ . An attempt to prepare  $\alpha$ -diaminohexoic acid from this failed through lack of material.

W. R.

**The Nature of Hofmann's Bromoacetamide.** MAURICE FRANÇOIS (*Compt. rend.*, 1909, 148, 173—176; *J. Pharm. Chim.*, 1909, [vi], 29, 145—151. Compare this vol., i, 13).—The substance to which Hofmann (Abstr., 1882, 950) ascribed the constitution  $\text{CH}_3\cdot\text{CO}\cdot\text{NHBr}\cdot\text{H}_2\text{O}$  has been prepared by evaporating below  $30^\circ$  an aqueous solution of acetamide and pure hypobromous acid. The conclusion is drawn that the compound is *acetamide hypobromite*,



and that Hofmann's bromoacetamide, which arises from this by dehydration, should be regarded as a secondary amide of hypobromous acid.

W. O. W.

**Action of Nitrogen on Commercial Barium Carbide.** OTTO KÜHLING and O. BERKOLD (*Zeitsch. angew. Chem.*, 1909, 22, 193—197).—The influence of barium chloride on the absorption of

nitrogen by a heated mixture of barium carbonate and charcoal has already been determined (Abstr., 1908, i, 143), and the investigation has been extended to barium carbide. Moissan (Abstr., 1894, i, 314) has already shown that this compound only combines with traces of nitrogen at 1200°, but the effect of other substances was not ascertained. The barium carbide used in the experiments had the following composition: Ba, 49.86; Ca, 17.11; Fe + Al, 2.62; "carbide" carbon, 7.62; Na, 0.85; Cl, 0.18; insoluble matter, 9.76; P, S, O, and CO<sub>2</sub>, 12.00% (by difference), and the material therefore probably contains both calcium and barium carbides as well as their oxides.

The absorption of nitrogen with this material begins at 500—600°, and there is an increase in the nitrogen absorbed as the temperature rises to 920—930°, when the maximum amount is absorbed, the percentage of cyanide formed at 920—930° being 18.4, that of cyanamide 19.4. With 10% barium chloride the maximum absorption is attained at this temperature also, but with 20 and 30% of added chloride the maximum had not been reached at 1120—1130°. With the larger amount of chloride at the latter temperature, the yield of cyanide was somewhat greater (21.6%), the yield of cyanamide somewhat less (17.9%).

W. R.

**Preparation of Cyanuric Acid from Carbamide.** REINHOLD VON WALTHER (*J. pr. Chem.*, 1909, [ii], 79, 126—128).—Cyanuric acid is obtained in 62% yield by heating carbamide with twice its weight of anhydrous zinc chloride at 220°, decomposing the cold product with hydrochloric acid, and recrystallising the precipitate from hot water.

C. S.

**Molybdenum Hexathiocyanate Salts.** ARTHUR ROSENHEIM (*Ber.*, 1909, 42, 149—152).—Largely polemical, A reply to Maas and Sand (Abstr., 1908, i, 961; compare also *ibid.*, i, 397, 513, 614). It is suggested that many of the thiocyanate values obtained by Sand and Maas are low, owing to the oxidising action of the nitric acid used.

When a thiocyanate is boiled with sodium hydroxide solution, a small amount of ammonia is liberated, but the amount is so small that the error introduced into the estimation of ammonia would scarcely affect the formula deduced from the experimental data.

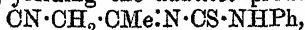
The sodium salt, Na<sub>3</sub>Mo(SCN)<sub>6</sub>·12H<sub>2</sub>O, forms golden-yellow crystals, and agrees in composition with the sodium salts of other complex thiocyanates.

J. J. S.

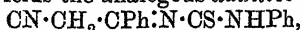
**Dimolecular Nitriles.** CARL W. HÜBNER (*J. pr. Chem.*, 1909, [ii], 79, 66—71).—This investigation was carried out with the object of filling some gaps in the chemistry of the dinitriles. Only one of the three condensation products obtained by von Meyer (Abstr., 1895, i, 582) by the action of phenylcarbimide on diacetonitrile [ $\beta$ -iminobutyronitrile] in benzene, namely, that having m. p. 148° (von Meyer gives m. p. 150°), is formed when ether is employed as the solvent. Benzacetodinitrile [ $\beta$ -iminophenylpropionitrile] and phenylcarbimide

also interact at the ordinary temperature in ethereal solution, yielding the analogous additive product, m. p.  $190^{\circ}$  (compare von Meyer, *loc. cit.*).

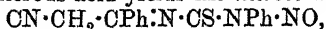
Phenylthiocarbimide reacts in a similar manner with  $\beta$ -iminobutyronitrile at  $140$ – $150^{\circ}$ , yielding the *additive* product,



which crystallises in small, orange-yellow needles, m. p.  $192^{\circ}$ .  $\beta$ -Imino-phenylpropionitrile yields the analogous *additive* product,



small, lemon-yellow needles, m. p.  $166^{\circ}$ , which, when heated under pressure at  $140$ – $150^{\circ}$  with alcoholic ammonia and lead oxide, yields the *guanidine* derivative,  $\text{C}_{16}\text{H}_{13}\text{N}_3\cdot\text{NH}$ , white leaflets, m. p.  $178^{\circ}$ , and when treated with nitrous acid yields the *nitroso*-derivative,



lemon-yellow needles, m. p.  $231^{\circ}$ .

The additive product obtained by heating  $\beta$ -iminobutyronitrile with dicyanodiamide at  $150^{\circ}$  (compare von Meyer, *loc. cit.*) has the formula  $\text{C}_6\text{H}_9\text{ON}_5$ ; it forms a *platinichloride*,  $(\text{C}_6\text{H}_9\text{ON}_5)_2\cdot\text{H}_2\text{PtCl}_6$ , which crystallises in golden-yellow needles, m. p.  $240^{\circ}$  (decomp.).

W. H. G.

**Action of Cyanogen on Sulphurous Acid.** DANIEL VORLÄNDER (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 92).—The action of cyanogen on sulphurous acid is similar to that of the halogens, but occurs more slowly:  $\text{C}_2\text{N}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} = 2\text{HCN} + \text{H}_2\text{SO}_4$ . With equivalent quantities in 0.1 to 0.2% solution, the amounts of cyanogen reduced and of sulphurous acid oxidised are initially equivalent. With a large excess of cyanogen, 94% of the sulphurous acid is oxidised after four to five days, but when the acid is in excess, only 23% of the cyanogen is reduced in seven to eight days.

C. S.

**Production of White Ferrous Ferrocyanide.** ROBERT L. TAYLOR (*Mem. Manchester Phil. Soc.*, 1908–09, 53, vi).—A creamy-white precipitate is obtained on adding potassium ferrocyanide to a solution of a ferrous salt which has been thoroughly reduced by hyposulphurous acid or sodium hyposulphite,  $\text{Na}_2\text{S}_2\text{O}_4$ . Hyposulphurous acid will even reduce precipitated Prussian blue to the white, ferrous compound.

R. J. C.

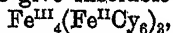
**Prussian Blue and Turnbull's Blue.** I. ERICH MÜLLER and THEOPHIL STANISCH (*J. pr. Chem.*, 1909, [ii], 79, 81–102).—In a solution containing ferric and ferrocyanogen ions or ferrous and ferricyanogen ions, the value of the equilibrium constant:

$$K = \frac{[\text{Fe}^{+++}][\text{FeCy}_6^{'''}]}{[\text{Fe}^{++}][\text{FeCy}_6^{''}]},$$

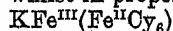
calculated from electrochemical data (Abegg, *Abstr.*, 1903, ii, 628; Schaum, *Abstr.*, 1900, ii, 2), is about  $10^{-6}$ , and therefore either solution will contain practically only ferrous and ferricyanogen ions. Consequently, the precipitates obtained from ferric chloride and potassium ferrocyanide, or from ferrous chloride and potassium ferricyanide, should be identical. The preceding reasoning, however, is inaccurate, since it assumes that all the ions remain in solution. The

authors agree with Hofmann (Abstr., 1905, i, 38) that the preceding precipitates are ferrocyanides, but deny that soluble and insoluble Prussian blue are identical respectively with soluble and insoluble Turnbull's blue. They object that Hofmann actually isolated the precipitates, which probably changed during the process, and only determined the iron and cyanogen or the ratio Fe : CN, which cannot give accurate information as to the composition of these complex and very similar blue ferrocyanogen compounds (compare Messner, Abstr., 1895, i, 486). The authors determine the compositions by a method which does not involve the separation of the precipitates from the mother liquor, and also estimate the ratio of ferrous to ferric iron and of ionised and non-ionised iron. In definite volumes of, for example, standard ferric chloride and standard potassium ferrocyanide the amounts of  $\text{Fe}^{+++}$  and of  $(\text{FeCy}_6)^{4-}$  are estimated by standard potassium permanganate before and after mixing, 0.1-molecular solutions being used to minimise the error due to any volume change on mixing. The decrease in the concentration of the ions represents the amounts which have disappeared from the solution to form the precipitate, but in consequence of the reaction:  $\text{Fe}^{+++} + (\text{FeCy}_6)^{4-} \rightleftharpoons \text{Fe}^{++} + (\text{FeCy}_6)^{3-}$ , it is not allowable to assume that the, for example, ferric iron which has disappeared from the solution occurs as such in the precipitate. However, the ratio of ferrous to ferric iron and of ionised to non-ionised iron can be estimated in the precipitate, and hence conclusions drawn as to its constitution.

The authors find that ferric chloride and potassium ferrocyanide in proportions exceeding 4 : 3 give insoluble Prussian blue,



whilst in proportions less than 1 : 1 the precipitate is a mixture of  $\text{KFe}^{\text{III}}(\text{Fe}^{\text{II}}\text{Cy}_6) + \text{K}_2\text{Fe}^{\text{II}}(\text{Fe}^{\text{II}}\text{Cy}_6)_2$ ; ferrous chloride and potassium ferri-cyanide in proportions exceeding 4 : 3 yield insoluble Turnbull's blue,  $\text{KFe}^{\text{II}}\text{Fe}^{\text{III}}_3(\text{Fe}^{\text{II}}\text{Cy}_6)_3$ , whilst in proportions less than 1 : 1,



is formed. The Roman numerals denote the valency of the iron.

C. S.

*cycloPropane*. ALFRED PARTHEIL (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 159).—*cycloPropane* can be prepared by heating together finely-divided zinc, amyl alcohol, and trimethylene bromide.

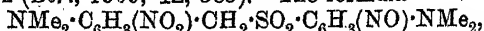
C. S.

**Introduction of Iodine into the Benzene Ring.** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1908, 58, 290—294. Compare Abstr., 1903, i, 450; Messinger and Vortmann, 1889, 1150; Wheeler and Jamieson, 1905, i, 350).—Fürth and Schwarz's statement (*Pflüger's Archiv*, 1908, 124, 113), that phenylalanine can yield an iodo-derivative when treated by Messinger and Vortmann's method, is refuted. Unaltered phenylalanine alone was recovered. Phenyl-acetic and phenylpropionic acids behave in a similar manner. The formation of iodo-derivatives only occurs when the benzene nucleus contains one or more hydroxyl groups. In certain reactions the pyrrole ring behaves as a phenol, for example, yields a tetraiodo-

derivative, and it is possible that the re-activity of tryptophan to iodine is due to the presence of the pyrrole group. J. J. S.

[Nitronitrosotetramethyldiaminophenylbenzylsulphone.]

ARTHUR BINZ (*Ber.*, 1909, 42, 385).—The formula

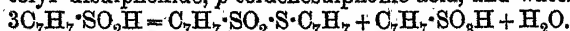


or a similar one in which the positions of the nitroso- and the nitro-groups are interchanged, is in better agreement with the analytical data for the nitroso-derivative obtained from tetramethyldiaminobenzylphenylsulphone than that originally given (*Abstr.*, 1908, i, 940). C. S.

The Action of Arsenites on Toluenesulphonyl Chloride. AUGUST GUTMANN (*Ber.*, 1909, 42, 480—483).—An aqueous solution of trisodium arsenite reacts with *p*-toluenesulphonyl chloride, yielding sodium toluenesulphinat and trisodium arsenate. It is suggested that the chloride first reacts with the alkali, yielding sodium hydroperoxide,  $\text{NaO} \cdot \text{OH}$ , which then oxidises the arsenite to arsenate. The formula  $\text{R} \cdot \text{SO} \cdot \text{OCl}$  for the sulphonyl chloride is accepted.

Sodium arsenite has no action on sodium *p*-toluenesulphonate. An alkaline solution of sodium sulphite reacts with the sulphonyl chloride in much the same manner as the arsenite, and is oxidised to sulphate. J. J. S.

*p*-Toluenesulphinic Acid. A. HEIDUSCHKA (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 170—172).—When ammonia is passed into an alcoholic or ethereal solution of *p*-toluenesulphinic acid, the corresponding ammonium salt is formed, whilst in benzene the reaction yields *p*-tolyl disulphoxide, *p*-toluenesulphinic acid, and water :

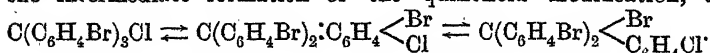


It is suggested that the ammonia acts as a base in the former, more concentrated, solutions, whilst in the dilute solution in benzene it acts as a catalyst. Primary amines show a similar behaviour; in equal molecular quantities, they react with *p*-toluenesulphinic acid to form salts, whilst if the amine is present in less than equal molecular quantity, the acid decomposes in accordance with the preceding equation. *p*-Toluenesulphinic acid decomposes in the same way in boiling water or by melting. The decomposition may throw some light on the nature of the highly-coloured products which are obtained by fusing amine toluenesulphinates (compare Meyer, *Abstr.*, 1901, i, 264). C. S.

Triphenylmethyl. XVIII. Tautomerism in the Triphenylmethane Series. MOSES GOMBERG (*Ber.*, 1909, 42, 406—417).—It was stated previously that triphenylmethyl chloride and its analogues exist in a benzenoid form and a quinonoid form (compare *Abstr.*, 1907, i, 504). This statement has been combated, however, by von Baeyer (*Abstr.*, 1907, i, 691) and by Tschitschibabin (*Abstr.*, 1907, i, 1022). Evidence is brought forward in the present communication in support of the author's view. A solution of tri-*p*-bromotriphenylmethyl chloride in liquid sulphur dioxide, which has been kept for

some time at 45—55° and then cooled, deposits colourless crystals, which analyses show to be composed of a mixture of tri-*p*-bromotriphenylmethyl chloride and 4-chloro-4':4''-dibromotriphenylmethyl bromide. In one experiment the isomorphous mixture contained about 85% of the latter substance.

There is little doubt that the transformation of the carbinyl chloride into the isomeric carbinyl bromide takes place owing to the intermediate formation of the quinonoid modification, thus:



Attempts to separate the pure carbinyl bromide by repeated crystallisation of the mixture were unsuccessful.

The action of liquid sulphur dioxide on 4-bromotriphenylmethyl chloride, 4:4'-dibromotriphenylmethyl chloride, 4-chloro-4':4''-dibromotriphenylmethyl chloride, and 4:4'-dichloro-4''-bromotriphenylmethyl chloride has also been studied. It is found in each case that a certain amount of the carbinyl chloride is converted into the isomeric carbinyl bromide, from which it follows that (1) part of the chlorine changes place with the bromine through the intermediate quinonoid form; (2) when the compound contains a brominated and a chlorinated benzene nucleus, it is the former which primarily changes into the quinonoid form under the influence of sulphur dioxide.

4-Chloro-4':4''-dibromotriphenylmethyl bromide forms colourless crystals, m. p. 174°. W. H. G.

**Action of Nitrosobenzene on Secondary Amines.** PAUL FREUNDLER and JULLARD (*Compt. rend.*, 1909, 148, 289—290. Compare Bamberger, *Abstr.*, 1896, i, 222).—Nitrosobenzene and secondary amines readily react to give azobenzene, together with smaller quantities of nitrobenzene, aniline, and possibly azoxybenzene. The greater part of the amine remains unaltered, but a portion is converted into the corresponding secondary hydroxylamine,  $\text{RR}'\text{N}\cdot\text{OH}$ . This reaction may be applied to differentiate between primary, secondary, and tertiary aliphatic amines. About 0.5 gram of the amine is mixed with nitrosobenzene, and when a red coloration appears, the product is distilled below 150° in a vacuum, if necessary. In the case of secondary amines, the distillate reduces silver nitrate solution in the cold, whilst with primary or tertiary amines no reducing agent is formed. A secondary hydroxylamine, however, appears to be formed when nitrosobenzene is heated for a long time with a tertiary amine.

W. O. W.

**Preparation of Esters of the Cyclic Series.** AUGUSTE BÉHAL (*Compt. rend.*, 1908, 147, 1478—1481).—Cyclic halogen derivatives react with organic acids, liberating hydrogen chloride, and giving rise to a cyclic ester. Thus, for example, benzyl chloride is converted into benzyl acetate when boiled for several hours with glacial acetic acid. The reaction proceeds more rapidly in presence of certain chlorides, notably those of antimony, bismuth, manganese, copper, and cobalt. The chlorides of iron, zinc, and tin have a similar action, but also

bring about the formation of resinous condensation products. The chlorides of magnesium, nickel, cadmium, mercury, chromium, barium, and strontium have no action, or else exercise a retarding effect.

Curves are given showing the influence of varying amounts of bismuth chloride, and of acetic acid on the velocity of the reaction.

W. O. W.

**Formation of Hydrogen Cyanide in the Action of Nitric Acid on Phenols and Quinones.** ALPHONSE SEYEWETZ and L. POIZAT (*Compt. rend.*, 1909, 148, 286—288).—Phenols and quinones containing an unsubstituted ortho- or para-position yield hydrogen cyanide when boiled with nitric acid (20%). With the exception of dimethylaniline and diethylaniline, no other aromatic compounds have been found to give the reaction, which is probably due to nitrous acid, since in presence of carbamide or aniline no hydrogen cyanide is evolved. A theoretical explanation of the reaction based on this fact is suggested.

W. O. W.

**1-Methylcyclohexan-2-ol and its Derivatives.** MURAT (*Ann. Chim. Phys.*, 1909, [viii], 16, 108—126).—A detailed account of the preparation and properties of certain esters, ethers, tertiary alcohols, and ethylenic hydrocarbons obtained from 1-methylcyclohexan-2-ol (Sabatier and Mailhe, *Abstr.*, 1905, i, 275).

The *hydrobromide* is less stable than the corresponding hydrochloride (Sabatier and Mailhe, *loc. cit.*), and has b. p. 118—120°/35 mm. and  $D^{20}$  1.240; the *barium salt* of the *sulphate*,  $(C_6H_{10}MeO \cdot SO_3)_2Ba$ , has m. p. 120°; the *propionate* has b. p. 189—190°,  $D^{20}$  0.9225,  $n_D^{20}$  1.443; the *butyrate* has b. p. 104°/20 mm.,  $D^{20}$  0.941,  $D^{20}$  0.930,  $n_D^{20}$  1.55; the *isobutyrate* has b. p. 102°/20 mm.,  $D^{20}$  0.940,  $D^{20}$  0.926,  $n_D^{20}$  1.441; the *valerate* has b. p. 112—113°/24 mm.,  $D^{20}$  0.939,  $D^{20}$  0.926,  $n_D^{20}$  1.448; the *isovalerate* has b. p. 110—112°/20 mm.,  $D^{20}$  0.9375,  $D^{21}$  0.926,  $n_D^{21}$  1.447; and the *benzoate* has b. p. 200°/55 mm.,  $D^{20}$  1.0325,  $D^{18}$  1.047,  $n_D^{18}$  1.521.

The ethers are readily obtained by the action of the alkyl iodide on the sodium derivative of the alcohol, and the following compounds were prepared: 2-ethoxy-1-methylcyclohexane, b. p. 156—158°/760 mm.,  $D^{20}$  0.9221,  $D^{20}$  0.912,  $n_D^{20}$  1.470; 2-amyl-1-methylcyclohexane, b. p. 177°,  $D^{20}$  0.936.

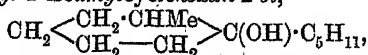
When 1-methylcyclohexan-2-one is heated with acetic anhydride during several days, it yields the *acetyl* derivative of a tetrahydrocresol,  $CH_2 \begin{matrix} \diagup CH_2 \cdot CHMe \\ \diagdown CH_2 - CH \end{matrix} COAc$ , b. p. 178°; the *tetrabromo*-derivative of the ketone,  $C_6H_5MeBr_4O$ , crystallises in needles and has m. p. 76°.

By the action of organo-magnesium derivatives on 1-methylcyclohexan-2-ol, the following tertiary alcohols were prepared:

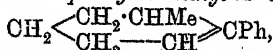
1-methyl-2-ethylcyclohexan-2-ol,  $CH_2 \begin{matrix} \diagup CH_2 \cdot CHMe \\ \diagdown CH_2 - CH_2 \end{matrix} CEt \cdot OH$ , b. p. 181—182°/745 mm.  $D^{20}$  0.9356,  $D^{20}$  0.9235,  $n_D^{20}$  1.458, forms an *acetyl*

derivative, which has b. p. 196—198°,  $D^0$  0.946, and on dehydration by means of zinc chloride yields a mixture of methylethylcyclohexenes, b. p. 149—153°,  $D^0$  0.829,  $D^{12}$  0.821, which is reduced by direct hydrogenation in the presence of nickel at 200°, yielding the methylethylcyclohexane, b. p. 151°,  $D^0$  0.7945,  $D^{20}$  0.784,  $n_D^{20}$  1.432;

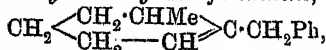
1-methyl-2-propylcyclohexan-2-ol,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{CPr} \cdot \text{OH}$ , b. p. 97—98°/34 mm.,  $D^0$  0.9276,  $D^{20}$  0.919,  $n_D^{20}$  1.48, forms an *acetyl* derivative, b. p. 107—110°/30 mm.,  $D^0$  0.9650,  $D^{20}$  0.956,  $n_D^{20}$  1.465, and on dehydration yields a mixture of ethylenic hydrocarbons, b. p. 167—170°,  $D^0$  0.8611,  $D^{20}$  0.848,  $n_D^{20}$  1.469; 1-methyl-2-tert-butylcyclohexan-2-ol,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CMe}_3$ , b. p. 93—96°/25 mm.,  $D^0$  0.9218,  $D^{26}$  0.908,  $n_D^{20}$  1.465, yields on dehydration a mixture of ethylenic hydrocarbons, b. p. 183—186°/750 mm.,  $D^0$  0.864,  $D^{27}$  0.836,  $n_D^{27}$  1.462; 1-methyl-2-isoamylcyclohexan-2-ol,



b. p. 118—120°/22 mm.,  $D^0$  0.912,  $D^{17}$  0.902,  $n_D^{17}$  1.462, yields on dehydration one or more ethylenic hydrocarbons, b. p. 205—208°,  $D^0$  0.851,  $D^{17}$  0.845,  $n_D^{17}$  1.471, which on direct hydrogenation in the presence of nickel at 230—250° is converted into a methylisoamylcyclohexane, b. p. 204°,  $D^0$  0.825,  $D^{17}$  0.812,  $n_D^{17}$  1.454; 2-cyclohexyl-1-methylcyclohexan-2-ol,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{C}_6\text{H}_{11}$ , b. p. 146—147°/30 mm. with decomposition,  $D^0$  0.978,  $D^{18}$  0.969,  $n_D^{18}$  1.501, is converted by the action of zinc chloride into an ethylenic hydrocarbon, b. p. 113—116°. Attempts to prepare corresponding tertiary alcohols by the action of 1-methylcyclohexan-2-ol on phenyl-, benzyl-, or tolylmagnesium iodide were unsuccessful, the ethylenic hydrocarbon being the only product isolated: 2-phenyl-1-methyl- $\Delta^2$ -cyclohexene,

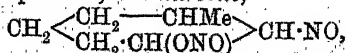


b. p. 128°/6 mm.; 2-benzyl-1-methyl- $\Delta^2$ -cyclohexene,

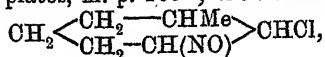


b. p. 170°/42 mm.,  $D^0$  0.99,  $D^{18}$  0.981,  $n_D^{18}$  1.453; 2-o-tolyl-1-methyl- $\Delta^2$ -cyclohexene,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH} \end{smallmatrix} \text{C} \cdot \text{C}_7\text{H}_7$ , b. p. 158—160°/12 mm.,  $D^0$  0.985,  $D^{20}$  0.961,  $n_D^{20}$  1.541.

The following derivatives of 1-methyl- $\Delta^2$ -cyclohexene are described: the *dichloro*-derivative, obtained by direct chlorination, has b. p. 123—125°/20 mm.,  $D^0$  1.2300; the *dibromo*-derivative, similarly prepared, b. p. 128°/35 mm.,  $D^0$  1.905; Knoevenagel has described a *dibromo*-derivative of hexahydrotoluene, b. p. 118°/20 mm. (Abstr., 1897, i, 608); the *nitrosate*,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 \cdot \text{C}(\text{NOH}) \end{smallmatrix} \text{CH} \cdot \text{ONO}_2$ , forms brilliant prisms, m. p. 104°; the *nitrosite*,



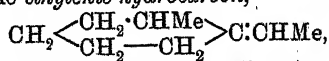
forms small, yellow plates, m. p. 103°; the *nitrosochloride*,



is unstable.

1-Methyl- $\Delta^1$ -cyclohexene yields a *dichloro*-derivative, b. p. 120°/20 mm.,  $D_0^{20}$  1.240; an unstable  *dibromo*-derivative, b. p. 126—130°/28 mm.; a *nitrosate*, m. p. 104°; a *nitrosite*, m. p. 102°, and a liquid *nitrosochloride*.

2-Chloro-1-methylcyclohexane reacts with magnesium, and the product condenses with acetaldehyde to form a secondary alcohol, which, on hydration, yields the *ethylenic hydrocarbon*,



b. p. 158°/760 mm.,  $D_0^{20}$  0.823,  $D_0^{20}$  0.81,  $n_D^{20}$  1.47.

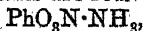
M. A. W.

**Chromo-isomeric Salts of *o*-Nitrophenols.** ANTONI KORCZYŃSKI (*Ber.*, 1909, 42, 167—177).—Hantzsch has shown (*Abstr.*, 1907, i, 207, 500) that the alkali salts of nitrophenols can be obtained in yellow, orange, and red modifications; the yellow and red salts are probably true isomerides, whereas the orange salts are solid solutions of the red and yellow varieties; however, the number of such isomeric salts prepared hitherto has been small. It is shown by the present investigation that the number of yellow salts of *o*-nitrophenols is quite as large as that of the red salts. The salts with amines are, as a rule, yellow, and do not differ appreciably from one another in shade; on the contrary, the red salts exhibit various shades of colour, depending on the nature of the alkali metal. Hantzsch has shown recently that the colour of the anion is not altered by union with an alkali metal in salt-formation; consequently, the yellow salts, which have precisely the same colour, must be chemically homogeneous, whereas the majority of the red salts of variable colour must be solid solutions of the red isomeride with small quantities of the yellow isomeride.

It has been found possible, by careful crystallisation from water or dilute alcohol, to separate the orange lithium salt of 2 : 4-dinitronaphthol into its red and yellow components.

The red and yellow salts are undoubtedly structurally identical, having the formula  $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{NO}_2 \end{array} \text{M}$ ; they are "chromo-isomerides," the exact nature of the isomerism being still unknown.

The *rubidium* ( $\frac{1}{2}\text{H}_2\text{O}$ ) and *lithium* ( $\frac{1}{2}\text{H}_2\text{O}$ ) salts of *o*-nitrophenol are orange; the *anhydrous* salts are red. The *ammonium* salt,



prepared by passing ammonia into the molten substance, is red, and quickly passes into the orange salt, which is also obtained by the absorption of ammonia in Ley and Wiegner's apparatus (*Abstr.*, 1905, i, 749) at the ordinary temperature; at -20°, the yellow salt,  $\text{PhO}_2\text{N} \cdot \text{NH}_3 \cdot \text{NH}_3$ , is obtained. The *methylamine*, *dimethylamine*, *trimethylamine*, *ethylamine*, *dipropylamine*, and *benzylamine* salts, precipitated from ethereal solution, all have the same yellow colour;

the *piperidine* salt forms yellow leaflets; the *piperazine* salt crystallises in yellow needles, m. p. 74—75°.

The *anhydrous lithium*, *sodium*, *potassium*, *rubidium*, and *silver* salts of *p*-bromo-*o*-nitrophenol are red; the *lithium* salt containing  $\text{H}_2\text{O}$  is orange, and the *sodium* salt ( $\frac{1}{2}\text{H}_2\text{O}$ ) is yellow when first precipitated; *ammonium* salts, similar to those of *o*-nitrophenol, were prepared. The salts with the organic bases mentioned above, with the exception of trimethylamine, have the same yellow colour; the *trimethylamine* salt is orange.

The *alkali* salts of 2:4-dibromo-*o*-nitrophenol are of a brighter red colour than the corresponding salts of *p*-bromo-*o*-nitrophenol; the *piperidine* and *methylamine* salts are yellow; the *ammonium*, *trimethylamine*, *dimethylamine*, *ethylamine*, *dipropylamine*, and *benzylamine* salts are orange; the *piperazine* salt,  $\text{C}_6\text{H}_3\text{O}_2\text{NBr}_2\cdot\text{C}_4\text{H}_{10}\text{N}_2$ , m. p. 160°, is orange; the *piperazine* salt,  $(\text{C}_6\text{H}_3\text{O}_2\text{NBr}_2)_2\cdot\text{C}_4\text{H}_{10}\text{N}_2$ , m. p. 185°, is scarlet.

The *lithium* and *sodium* salts of *o*-nitro-*p*-cresol, when prepared at -20°, are orange; the *potassium* ( $\frac{1}{2}\text{H}_2\text{O}$ ), *rubidium*, and *caesium* ( $1\text{H}_2\text{O}$ ) salts are red, as is also the *sodium* salt when prepared at the ordinary temperature; the *thallium* and *ammonium* salts are orange; the salts with organic bases are yellow.

The *lithium* ( $2\text{H}_2\text{O}$ ) and *potassium* ( $1\text{H}_2\text{O}$ ) salts of bromo-*o*-nitro-*p*-cresol are blood-red; the *anhydrous lithium* salt is yellow; the *sodium*, *benzylamine*, *piperazine*, and *ethylamine* salts are orange; the *methylamine*, *dimethylamine*, *trimethylamine*, and *piperidine* salts are yellow.

The *lithium* salt of *p*-chloro-*o*-nitrophenol is orange, but the *sodium* ( $1\text{H}_2\text{O}$ ) salt is red; the *methylamine*, *dimethylamine*, *trimethylamine*, *ethylamine*, *piperidine*, and *piperazine* salts are yellow.

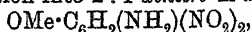
The *sodium* salt of  $\alpha$ -nitro- $\beta$ -naphthol, precipitated at low temperatures, is yellow, but quickly changes into the stable, orange form. The *dimethylamine*, *ethylamine*, and *benzylamine* salts are yellow.

The *lithium* ( $1\text{H}_2\text{O}$ ) and *sodium* salts of 3:5-dinitro-*p*-cresol are orange; the *anhydrous potassium*, *rubidium*, and *caesium* salts are red.

The *ammonium*, *methylamine*, *ethylamine*, *benzylamine*, *dimethylamine*, and *trimethylamine* salts of 2:4-dinitronaphthol are yellow; the *piperazine* salt crystallises in large, orange prisms, but the powdered substance is yellow; the *sodium*, *potassium*, *rubidium*, *caesium*, and *thallium* salts are orange; the *lithium* salt ( $1\text{H}_2\text{O}$ ) is orange, and loses its water at 160° without changing colour; the anhydrous salt absorbs  $1\text{H}_2\text{O}$  from the air, and becomes carmine-red. When a solution of the salt in dilute alcohol is cautiously concentrated at 70°, it deposits at first a *carmine* salt,  $1\text{H}_2\text{O}$ , as microscopic leaflets or needles, after which a *yellow* salt,  $1\text{H}_2\text{O}$ , crystallises out in needles; both salts when dehydrated pass into the orange variety; the yellow modification generally passes spontaneously into the red form. Equivalent solutions of the two salts have the same colour and are equally intense.

W. H. G.

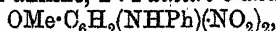
**Derivatives of 2:3:4-Trinitroanisole.** JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 85—88. Compare Abstr., 1908, i, 978; Meldola, *Trans.*, 1902, 81, 993).—Derivatives of 2:3:4-trinitroanisole are described. The parent substance was prepared by treating 2:3-dinitroanisole with a mixture of sulphuric acid and fuming nitric acid. Crystallised from alcohol, it has m. p. 155°. Its constitution was determined by conversion into 2:4-dinitro-*m*-anisidine,



by heating in alcoholic solution with the equivalent quantity of ammonia in a sealed tube in the water-bath. It separates from alcohol in yellow crystals, m. p. 167°. When this compound is diazotised in sulphuric acid solution, and the diazo-solution poured into boiling alcohol, 2:4-dinitroanisole is obtained, proving that the parent substance is 2:3:4-dinitroanisole.

With methylamine in alcoholic solution, 2:3:4-trinitroanisole yields 2:4-dinitro-3-methylaminoanisole,  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{NHMe})(\text{NO}_2)_2$ , which separates from alcohol in yellow crystals, m. p. 130°. When this compound is dissolved in a mixture of nitric and sulphuric acids and the solution poured into water, 3-nitromethylamino-2:4:6-trinitroanisole,  $\text{OMe}\cdot\text{C}_6\text{H}(\text{NMe}\cdot\text{NO}_2)(\text{NO}_2)_3$ , separates as a sticky mass, which crystallises from methyl alcohol in colourless crystals, m. p. 99° (Romburgh, *Abstr.*, 1889, 971).

When 2:3:4-trinitroanisole in alcoholic solution is boiled with the equivalent quantity of aniline, 2:4-dinitro-3-anilinoanisole,



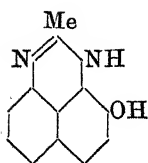
is formed. It crystallises from alcohol in reddish-brown crystals, m. p. 152°.

When 2:3:4-trinitroanisole is heated with aqueous sodium carbonate, the nitro-group at 3 is replaced by hydroxyl, yielding the monomethyl ether of 2:4-dinitroresorcinol,  $\text{OMe}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OH}$ , which separates from water in light yellow crystals, m. p. 108°.

The nitro-group at 3 in 2:3:4-trinitroanisole is replaced by methoxyl by heating with sodium methoxide in methyl alcohol solution, with formation of the dimethylether of 2:4-dinitroresorcinol, identical with that obtained by Kauffmann and Franck (*Abstr.*, 1907, i, 1092). Crystallised from alcohol, it has m. p. 73°. When freshly prepared it is colourless, but direct sunlight turns it reddish-brown.

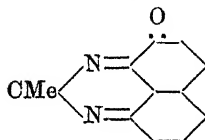
Treatment of 2:3:4-trinitroanisole with sodium ethoxide, with a view to replacing the nitro-group at 3 by ethoxyl, resulted in a complex reaction which is under investigation. A. J. W.

**Derivatives of 8-Amino- $\beta$ -naphthol.** FRIEDRICH KEHRMANN and E. F. ENGELKE (*Ber.*, 1909, 42, 350—353).—During the course of unsuccessful attempts to prepare 8-acetylamino- $\beta$ -naphthaquinone, the following new compounds have been obtained. 8-Acetylamino- $\beta$ -naphthol,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{NHAc}$ , m. p. 164—165°, obtained from the aminonaphthol and acetic anhydride, is converted by sodium nitrite and dilute sulphuric acid into 1-nitroso-8-acetylamino- $\beta$ -naphthol, m. p. 133—134° (decomp.), which separates from boiling water in golden-yellow needles. The nitroso-compound, by treatment with 3 parts of stannous chloride in 20% hydrochloric acid for twelve



(I.)

re-converted by reducing agents into the original salt, and is probably 9-quinol-2-methylperimidine (formula II).



(II.)

hours, yields yellow crystals of the *hydrochloride* of 9-hydroxy-2-methylperimidine (formula I; compare Sachs, *Chem. Zeit.*, 1908, 30, IX for nomenclature).

Oxidation of an aqueous solution of the salt by sulphuric and chromic acids at 0° yields a substance,  $C_{12}H_8ON_2$ , m. p. 175° (decomp.), which crystallises in orange-yellow prisms, is re-converted by reducing agents into the original salt, and is probably 9-quinol-2-methylperimidine (formula II).

C. S.

**Substitution of Zinc by Magnesium in the Synthesis of Unsaturated Alcohols.** W. JAWORSKY (*Ber.*, 1909, 42, 435—438. Compare *Abstr.*, 1908, i, 753).—It is found that much

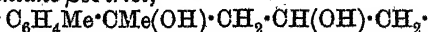
better yields are obtained by substituting magnesium for zinc in the preparation of unsaturated alcohols by Saytzeff's method. A mixture of allyl bromide and the ketone in equivalent proportions is slowly added to magnesium ribbon (which has previously been treated for a short time with an ethereal solution of allyl bromide) immersed in absolute ether. The reaction product is subsequently treated with dilute acid, and the alcohol dried and fractionally distilled.

*Diphenylallylcarbinol*,  $C_{16}H_{18}O$ , prepared from benzophenone, allyl bromide, and magnesium, is a colourless liquid, b. p. 182—183°/32 mm. The following substances were also prepared: a viscid, yellow oil, b. p. 169°/27 mm., from piperonaldehyde; an oil, b. p. 266—272°/760 mm., from furfuraldehyde; a limpid liquid, b. p. 168—170°/760 mm. (decomp.), from mesityl oxide; a yellow oil, b. p. 165°/760 mm. (decomp.), from benzylideneacetone; a viscid, yellow oil, decomposing when boiled under 22 mm. pressure, from benzil.

W. H. G.

**Action of Magnesium on a Mixture of *p*-Tolyl Methyl Ketone and Allyl Iodide.** E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1685—1691).—*p*-Tolylmethylallylcarbinol,  $C_6H_4Me \cdot CMe(C_3H_5) \cdot OH$ , obtained together with a small proportion of diallyl by the action of magnesium on a mixture of *p*-tolyl methyl ketone with allyl iodide or bromide, is a viscous, colourless liquid with a camphor-like odour and an intensely bitter taste, b. p. 128°/15 mm., 132.5—133°/30 mm., 237—240°/760 mm.,  $D_4^{25}$  0.9807,  $D_4^{15}$  0.9832,  $n_D^{25}$  1.5236. The alcohol readily unites with bromine (2 atoms), giving a syrupy compound, which rapidly decomposes with evolution of hydrogen bromide.

*$\beta$ -p-Tolylpentane- $\beta$ -triol,*



prepared by oxidising *p*-tolylmethylallylcarbinol by means of 1% potassium permanganate solution, crystallises from a mixture of ether and light petroleum in colourless needles, m. p. 101—103°.

*$\beta$ -p-Tolyl- $\beta$ -methylhydracrylic acid*,  $C_6H_4Me \cdot CMe(OH) \cdot CH_2 \cdot CO_2H$ , obtained by oxidising *p*-tolylmethylallylcarbinol by means of 4% potassium permanganate solution, forms acicular crystals, m. p.

102—104°. The *silver* salt, which is readily soluble in hot water, and the *calcium* and *barium* ( $+2\text{H}_2\text{O}$ ) salts were prepared.

T. H. P.

**Distribution of Cholesterol and its Allies.** CHARLES DORÉE (*Bio-Chem. J.*, 1909, 4, 72—106).—Cholesterol is widely distributed in the animal kingdom, being found in representatives of all classes examined. In one or two cases analogous substances take its place, spongosterol in sponges, and so forth. The amount present varies, and the results are stated quantitatively. The same wide distribution of the phytosterols is found in the vegetable world, and these substances are probably the source of cholesterol in animals. The whole group consists of isomeric or closely related substances exhibiting the unsaturated linking and the hydroxyl group which are necessary for their antitoxic action.

W. D. H.

**Fatty Acid Combinations with Cholesterol.** CHARLES P. WHITE (*Proc. Physiol. Soc.*, 1908, vi; *J. Physiol.*, 38).—Cholesterol forms loose combinations with fatty acids which differ from true esters. Those with the fatty acids higher than hexoic can be obtained as fluid crystals, and give "myelin forms" and, finally, an emulsion of anisotropic globules on the addition of water. Similar combinations are formed by cholesterol with lecithin, cetyl alcohol, glycerol, mono- and di-palmitin, but not with triglycerides. The globules found in certain tissues (adrenal cortex) are of similar nature. Cholesterol may thus assist in the emulsification, absorption, and transference of fats.

W. D. H.

**Agrosterol: a Cholesterol Substance in Soils.** OSWALD SCHREINER and EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1909, 31, 116—118).—The authors have isolated a cholesterol substance from Marshall clay (a soil containing 10.6% of organic matter and 0.51% of nitrogen), obtained from North Dakota, by extraction with alcohol and suitable treatment of the extract with ether and alcohol. The substance crystallises from ether in colourless needles, m. p. 237°, and from 80% alcohol in flat plates containing water of crystallisation. It is proposed to name this substance *agrosterol*, since it gives Liebermann's cholesterol reaction and has the formula  $\text{C}_{26}\text{H}_{44}\text{O}$ .

W. H. G.

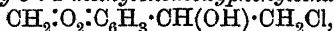
**New Synthesis of Adrenaline and Allied Compounds.** KARL BÖTTCHER (*Ber.*, 1909, 42, 253—266).—Barger and Jowett (*Trans.*, 1905, 87, 970) were unable to convert  $\alpha\beta$ -dibromo-3:4-methylenedioxyphenylethane by means of phosphorus pentachloride into a chlorinated compound which could be decomposed to a dihydroxy-compound on hydrolysis with water; they obtained, in addition to  $\beta$ -bromo- $\alpha$ -hydroxy-3:4-methylenedioxyphenylethane, a dibromohydrin, m. p. 158°.

When, however,  $2\frac{1}{2}$  to 3 mols. of phosphorus pentachloride are allowed to act on the dibromide for a considerable time at 105°, a chlorinated product is obtained, which is decomposed by water into

$\beta$ -bromo- $\alpha$ -3 : 4-trihydroxyphenylethane. The halogen in this compound may be replaced by the NHMe-group, forming adrenaline.

By a similar series of reactions,  $\psi$ -safrole,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CMe:CH}_2$ , and isosafrole,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH:CHMe}$ , or their dichlorides or chlorohydrins, can be converted into methyladrenaline. A monobromo-adrenaline is obtained from the dibromohydrin, m. p.  $158^\circ$ . These three substituted adrenalines exhibit no pharmacological activity.

$\beta$ -Chloro- $\alpha$ -hydroxy-3 : 4-methylenedioxyphenylethane,

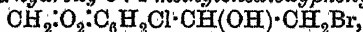


crystallises in long needles, m. p.  $95^\circ$ ; it is prepared by acting with chlorine on a cooled solution of vinylcatechol methylene ether in carbon tetrachloride, whereby the  $\alpha\beta$ -dichloroethane is first obtained as a reddish-coloured oil, and this is subsequently hydrolysed by means of a mixture of acetone and water.

$\beta$ -Chloro- $\alpha$ -3 : 4-trihydroxyphenylethane,  $\text{C}_6\text{H}_3(\text{OH})_2\text{:CH(OH)\cdot CH}_2\text{Cl}$ , is prepared from the methylene ether by prolonged heating with a large excess of phosphorus pentachloride, and subsequent hydrolysis with a mixture of acetone and water. It forms needles which decompose about  $100^\circ$ , gives an intense green coloration with ferric chloride, and soon decomposes when kept exposed to the action of light. The carbonic ester,  $\text{CO:O}_2\text{:C}_6\text{H}_3\text{:CHCl\cdot CH}_2\text{Cl}$ , formed as an intermediate product in its preparation, may be isolated as an oil, b. p.  $190^\circ/13$  mm.

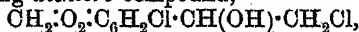
$\beta$ -Bromo- $\alpha$ -3 : 4-trihydroxyphenylethane is prepared from the corresponding methylene ether in an analogous manner. It crystallises in clusters of small needles, m. p.  $92\text{--}93^\circ$ , decomposing to a dark violet substance, shows the same intense green coloration with ferric chloride, and decomposes even more easily than the chloro-compound. Either compound when dissolved in alcohol and shaken with a large excess of aqueous methylamine is converted into adrenaline. Although the compound prepared in this manner has not yet been obtained in the form of crystalline salts, it is very active physiologically.

Chloro- $\beta$ -bromo- $\alpha$ -hydroxy-3 : 4-methylenedioxyphenylethane,



prepared by the action of sulphuryl chloride on bromohydroxy-methylenedioxyphenylethane, crystallises in well-formed, long needles, m. p.  $128\text{--}129^\circ$ . The halogen cannot be removed by heating with aqueous acetone. The acetate forms crystals, m. p.  $89^\circ$ .

The corresponding dichloro-compound,



obtained by the action of sulphuryl chloride on chlorohydroxy-methylenedioxyphenylethane, separates in needles, m. p.  $126\text{--}127^\circ$ .

A tetrabromo-compound, prepared by the action of bromine vapour on  $\alpha\beta$ -dibromomethylenedioxyphenylethane, forms tiny crystals, m. p.  $141\text{--}143^\circ$ .

$\psi$ -Safrole chlorohydrin,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CMe(OH)\cdot CH}_2\text{Cl}$ , prepared by the action of chlorine on  $\psi$ -safrole, is a faintly yellow-coloured oil. It is converted by treatment with phosphorus pentachloride and subsequent hydrolysis with water into dihydroxyphenyl- $\psi$ -allylchlorohydrin,  $\text{C}_6\text{H}_3(\text{OH})_2\text{:CMe(OH)\cdot CH}_2\text{Cl}$ , a thin oil from which  $\alpha$ -methyladrenaline is obtained as a bright golden-brown powder.

*iso*Safrole dichloride,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHCl}\cdot\text{CHMeCl}$  (Hoering, Abstr., 1905, i, 903), is an oil, b. p. 164—166°/11 mm., 270°/760 mm. with much decomposition.

$\beta$ -Chloro- $\alpha$ -hydroxy- $\alpha$ -(3:4)-dioxyphe~~n~~ylpropane,  
 $\text{C}_6\text{H}_3(\text{HO})_2\cdot\text{CH}(\text{OH})\cdot\text{CHMeCl}$ ,

forms needles, m. p. 104—105° (decomp.), and when shaken with methylamine gives rise to  $\beta$ -methyladrenaline, a bright yellow powder.

$\beta$ -Bromo- $\alpha$ -hydroxy-3:4-dioxybromophenylethane, m. p. 157—158°, is conveniently prepared by the action of bromine on a solution of vinylcatechol methylene ether in carbon tetrachloride. The *acetate* has m. p. 100—101°. Oxidation with permanganate forms monobromopiperonylic acid, m. p. 201—202°.

$\beta$ -Bromo- $\alpha$ -hydroxy-3:4-carbonatobromophenylethane,  
 $\text{CO}:\text{O}_2:\text{C}_6\text{H}_2\text{Br}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}$ ,

forms glistening plates, m. p. 107°, and is converted when left in contact with acetone and water into  $\beta$ -bromo- $\alpha$ -3:4-trihydroxybromophenylethane,  $\text{C}_6\text{H}_2\text{Br}(\text{OH})_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}$ , which crystallises in lancet-like needles, m. p. 121—123°, and gives a green coloration with ferric chloride in aqueous solution.

$\alpha$ -3:4-Trihydroxy- $\beta$ -methylaminobromophenylethane,  
 $\text{C}_6\text{H}_2\text{Br}(\text{OH})_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NHMe}$ ,

is obtained by the action of methylamine on the above as a light brown powder.

E. F. A.

New Syntheses of Adrenaline and Allied Compounds. HERMANN PAULY (*Ber.*, 1909, 42, 484—485).—It is claimed that Böttcher (preceding abstract) had not proved that the product obtained by him is adrenaline.

J. J. S.

Polynaphthenic Acids. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chm. Soc.*, 1908, 40, 1757—1774).—Oxidation by means of air in presence of alkali serves as a means of characterising hydrocarbons and of estimating them in mixtures such as naphtha and its fractional distillates. Under the above conditions, saturated hydrocarbons give a negligible quantity of liquid oxidation products, whilst naphthenes give polynaphthenic or asphaltogenic acids, which are syrupy liquids, D 1.2, incapable of crystallising, and are not reduced to more highly hydrogenated compounds by means of sodium amalgam. These acids give the red coloration yielded by ketones with sodium nitrosulphide, reduce ammoniacal silver nitrate solution and Fehling's solution, and decompose on distillation, even under greatly reduced pressure. They are soluble in alcohol, benzene, chloroform, ether, and carbon disulphide.

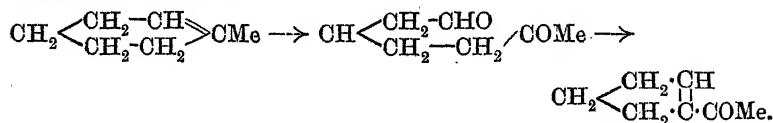
Oxidation of the fraction of "Meteor" kerosine, b. p. 169—171°, consisting of one of the isomeric decanaphthenes, yielded a dibasic acid which, on analysis and on determination of the molecular weight cryoscopically and ebullioscopically, was found to have the formula  $\text{C}_{20}\text{H}_{32}\text{O}_4$ .

T. H. P.

$\Delta^1$ -Cyclopentene as an Oxidation Product of  $\Delta^1$ -cyclo-Hexene- $\alpha$ - $\beta$ -dicarboxylic Acid. WILLIAM H. PERKIN, jun. and OTTO WALLACH (*Ber.*, 1909, 42, 145—149. Compare Wallach, Abstr., 1906, i, 176; 1907, i, 616; 1908, i, 426).—The ketone  $\text{C}_7\text{H}_{10}\text{O}$  (Harding, Haworth,

and Perkin, Trans., 1908, 93, 1946) has been definitely proved to be acetyl*cyclopentene*.

The fact that both  $\Delta^1$ -*cyclohexeneacetic acid* and methyl- $\Delta^1$ -*cyclohexene* yield acetyl*cyclopentene* when oxidised at 0° with permanganate proves that in this reaction a rupture of the six-membered ring occurs, and is followed by a closing of the ring to give a *cyclopentene* derivative:



The possibility of such a reaction must be borne in mind when the constitution of a cyclic compound is based on an examination of the products of oxidation with permanganate. J. J. S.

**Isomeric Cinnamic Acids.** EINAR BIILMANN (*Ber.*, 1909, 42, 182—188. Compare Liebermann, Abstr., 1903, i, 255; Erlenmeyer, jun., Abstr., 1906, i, 429).—It is shown that *allocinnamic acid*, m. p. 68°, *isocinnamic acid*, m. p. 57° (compare Liebermann, Abstr., 1890, 1417), and *isocinnamic acid*, m. p. 38—46° (Erlenmeyer, sen., Abstr., 1891, 200), are chemically identical and are not chemical isomerides. The three substances are trimorphous, and may be converted one into the other by simply melting the solid substance, cooling the fused mass, and inoculating with the acid required. Thus the *isocinnamic acid*, m. p. 41°, may be obtained from *allocinnamic acid* by melting this acid in a tube closed with a cotton-wool plug and subsequently cooling the fused mass in a freezing mixture; if this is heated to about 44° and inoculated with the *isocinnamic acid*, m. p. 58°, the whole mass solidifies and melts then at 58°. *alloCinnamic acid* may be obtained from this in the same manner.

Special precautions must be taken in crystallising *isocinnamic acid*, m. p. 58°, in order to prevent inoculation with *allocinnamic acid*. Thus, in order to crystallise the former in a room "infected" with the latter, it must be dissolved and the solution boiled after closing the vessel with a cotton-wool plug. This probably explains why Liebermann, having once obtained *allocinnamic acid*, could not again obtain *isocinnamic acid*, m. p. 58°.

The *isocinnamic acid*, m. p. 41°, when treated with light petroleum appears at first to dissolve, but in a few seconds the acid, m. p. 58°, crystallises out from the solution. W. H. G.

**Remark on Biilmann's Discussion of the Isomeric Cinnamic Acids.** EMIL ERLENMEYER, jun. (*Ber.*, 1909, 42, 521—522. Compare Biilmann, preceding abstract).—Polemical. Biilmann's observations are not wholly in accord with those of Liebermann and the author on the three acids from *allocinnamic acid*: the fact that *allocinnamic acid* can be separated from the *iso*-acid is held to be against the idea of polymorphism. W. R.

Separation of Synthetic Cinnamic Acid into its Isomeric Components and their Re-combination into the Synthetic Acid. EMIL ERLNMEYER, jun. [with O. HERZ] (*Ber.*, 1909, 42, 502—513. Compare Abstr., 1906, i, 21, 176; 1907, i, 318).—It has already been shown that the synthetic acid is a mixture of storax-cinnamic acid and another acid of m. p. 128°. It has now been demonstrated that this admixed acid is not benzoic, thienylacrylic, or an alkyl- or methoxy-cinnamic acid. Fractional crystallisation is not a suitable method for obtaining this acid, but it may be obtained by fractional distillation of the ethyl esters. Ethyl storax-cinnamate has b. p. 148—151°/20 mm., whereas the ethyl ester of the synthesised acid has b. p. 152—165°/20 mm., and leaves in addition a considerable residue (10—20%). This distillate on careful refractionation gave a separation; the fraction of lowest b. p. on hydrolysis yielded "storax" acid, that of highest b. p. gave the acid, m. p. 128°, *heterocinnamic acid*. Moreover, this hetero-acid, like the cinnamic acid from storax, exists in two forms. The residue just mentioned distils at 269—271°, and on hydrolysis with cold 20% alcoholic potassium hydroxide a salt separates which yields *hetero-β-cinnamic acid* as an amorphous precipitate, m. p. 128°. It exhibits all the chemical properties of a cinnamic acid, and it separates from ethereal solution in a characteristic chalky form. It dissolves in 7—7·30 parts of 75% alcohol, whereas storax-α-cinnamic acid dissolves in 16·67 parts, and storax-β-acid in 11·31.

The hetero-β-cinnamic acid on repeated dissolution in petroleum is converted into the α-modification, which crystallises in glistening, thin leaflets, m. p. 130—131°. It dissolves in 9·40—9·54 parts of 75% alcohol, and by re-solution in water or alcohol it is converted into the chalky isomeride.

When storax-α- and hetero-α-acids are mixed in equal proportions and crystallised from ether, the synthetic acid is reformed, also the two α-acids form mixed crystals. The hetero-β-cinnamic acid does not give a single substance; on the bottom of the vessel the β-acid is seen, and glistening leaflets on the sides. W. R.

Salt Formation and Addition Reactions of the Isomeric Acids obtained from Synthetic Cinnamic Acid, and Demonstration of their Different Chemical Behaviour. EMIL ERLNMEYER, jun. [with O. HERZ and G. HILGENDORFF] (*Ber.*, 1909, 42, 513—521. Compare preceding abstract).—The salts of storax-α- and hetero-β-cinnamic acid exhibit strong resemblances, yet the original acids are recovered from them unchanged; thus the diphenyloxyethylamine salt of storax-α-acid crystallises in slender needles, m. p. 177°; the salt of the hetero-β-acid crystallises similarly, m. p. 172°. Brucine forms an acid and a normal salt with the hetero-β-acid, which are very similar to those of the storax acid; they are, however, somewhat more soluble, and differ slightly in optical rotatory power (20'). A non-crystallisable syrup was obtained by mixing the two acids and attempting to prepare a solid brucine salt.

A potassium hydrogen storax-α-cinnamate,  $C_{15}H_{15}O_4K$ , is obtained from 2 mols. acid and  $\frac{1}{2}$  mol. potassium carbonate, which is acid to test

paper and stable; it crystallises from alcohol (75%) in long crystals; the *potassium hydrogen* salt from the synthetic acid forms leaflets, and the similar salt from the hetero- $\beta$ -acid is amorphous. Benzoic acid also forms a potassium hydrogen salt.

The properties described hitherto as descriptive of the different isomerides have all been physical. However, chemical differences also exist; the dibromide from storax- $\alpha$ -acid is formed more readily than that from hetero- $\beta$ -acid; the ester of storax- $\alpha$ -acid is more rapidly hydrolysed than the hetero- $\beta$ -ester, and these acids may be separated by taking advantage of the fact that hypochlorous acid forms an additive compound much more slowly with the hetero- than with the storax-acid.

The storax acid dibromide crystallises in stout crystals, m. p. 205—206°; the hetero-dibromide forms thin leaflets, m. p. 204°, whilst the dibromide from the synthetic acid is intermediate in crystalline character. By Liebermann's method all these dibromides give the original acids.

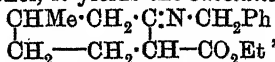
Synthetic cinnamic acid, when fractionally precipitated from its aqueous sodium salt solution, is separated into hetero- $\alpha$ - and - $\beta$ - and storax- $\alpha$ -acids, which shows that these acids differ in strength also.

The nature of the isomerism is discussed shortly, and the opinion expressed that these isomeric phenomena are due to differences in the benzene nucleus.

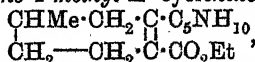
W. R.

**Action of Ammonia and Amines on Tetrahydrosalicylic Esters.** ARTHUR KÖTZ and B. MERKEL (*J. pr. Chem.*, 1909, [ii], 79, 102—125).—Ethyl 3-amino-1-methylcyclohexane-4-carboxylate (Abstr., 1906, i, 88), which does not react with aqueous or methyl alcoholic ammonia, yields, with boiling aniline, alcohol and the substance,  $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NH} \\ | \quad \quad | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{C} \cdot \text{CO} \end{array}$ , m. p. 261° (decomp.), and, by heating alone at 280°, forms alcohol and the bimolecular compound,  $\text{C}_{16}\text{H}_{22}\text{O}_2\text{N}_2$ , m. p. above 300°.

Ethyl 1-methylcyclohexan-3-one-4-carboxylate, when heated with aminocyclohexane, yields a substance,  $\text{C}_8\text{H}_{11}\text{ON}_2$ , m. p. 264°, which appears to be identical with the preceding. With boiling aniline (1 mol.), the ester yields the *anilinoanilide*,  $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NHPh} \\ | \quad \quad | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{C} \cdot \text{CO} \cdot \text{NHPh} \end{array}$ , m. p. 130°, whilst with benzylamine at the ordinary temperature, with or without methyl alcohol, it yields the substance,

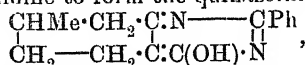


m. p. 61°, into which the attempt to introduce a second  $\text{N} \cdot \text{CH}_2\text{Ph}$  group was unsuccessful. Ethyl 1-methylcyclohexan-3-one-4-carboxylate reacts (a) with the calculated amount of piperidine at the b. p. to form *ethyl 3-piperidino-1-methyl- $\Delta^3$ -cyclohexene-4-carboxylate*,



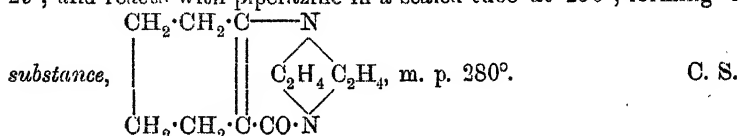
m. p. 123°; (b) with carbamide in warm dilute sodium ethoxide solution

to form the substance,  $\begin{array}{c} \text{CHMe} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{C} \cdot \text{CO} \cdot \text{NH} \end{array}$ ; (c) with methylalcoholic benzenylamidine to form the quinazoline derivative,

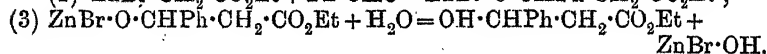
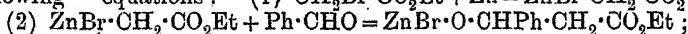


m. p. 227°, and (d) with piperazine at 150° to form the substance,  $\text{CH}_2 \left\langle \begin{array}{c} \text{CHMe} - \text{CH}_2 \\ \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{Et}) \end{array} \right\rangle \text{C} \cdot \text{C}_4\text{N}_2\text{H}_8 \cdot \text{C} \left\langle \begin{array}{c} \text{CH}_2 - \text{CHMe} \\ \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \end{array} \right\rangle \text{CH}_2$ , m. p. 216°.

Ethyl cyclohexan-2-one-1-carboxylate, when heated with aniline, yields ethyl 2-anilino- $\Delta^1$ -cyclohexene-1-carboxylate,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{NHPh} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$ , m. p. 29°, and reacts with piperazine in a sealed tube at 250°, forming the

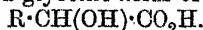


**Synthesis of  $\beta$ -Hydroxy- $\beta$ -phenylpropionic Acid.** W. N. ANDRIEWSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1635—1638).—In presence of zinc, benzaldehyde and ethyl bromoacetate react, giving ethyl  $\beta$ -hydroxy- $\beta$ -phenylpropionate (compare Daïn, *J. Russ. Phys. Chem. Soc.*, 1890, 22, 44), the changes being represented by the following equations: (1)  $\text{CH}_3\text{Br} \cdot \text{CO}_2\text{Et} + \text{Zn} = \text{ZnBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ ;



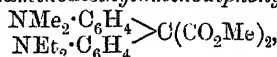
T. H. P.

**Condensation of Mesoxalic Esters with Aromatic Tertiary Amines.** ALFRED GUYOT and EDMOND MICHEL (*Compt. rend.*, 1904, 148, 229—232).—Ethyl mesoxalate readily undergoes condensation with aromatic tertiary amines. Ethyl dimethyl-*p*-aminophenyltartronate,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH})(\text{CO}_2\text{Et})_2$ , prepared by heating an acetic acid solution of dimethylaniline with ethyl mesoxalate for thirty minutes, forms colourless leaflets, m. p. 76.5°. The following compounds have also been prepared: Methyl *p*-dimethylaminophenyltartronate, prisms, m. p. 115°; ethyl *p*-diethylaminophenyltartronate,  $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH})(\text{CO}_2\text{Et})_2$ , prisms, m. p. 45°; the methyl ester, needles, m. p. 103°. On hydrolysis with aqueous potassium hydroxide, these substances form the corresponding acids, which are unstable and have been converted into aldehydes, and also into glyoxylic acids of the type  $\text{R} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , and glycollic acids of the type



Under the influence of phosphoryl chloride, the foregoing esters undergo further condensation with aromatic tertiary amines. Thus ethyl *p*-dimethylaminophenyltartronate and dimethylaniline yield ethyl tetramethyldiaminodiphenylmalonate,  $\text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2(\text{CO}_2\text{Et})_2$ , white leaflets, m. p. 93°. The following compounds have been prepared in the same way: Ethyl dimethylaminodiphenyl-

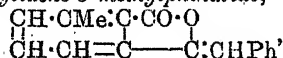
malonate,  $\frac{\text{NMe}_2 \cdot \text{C}_6\text{H}_4}{\text{NEt}_2 \cdot \text{C}_6\text{H}_4} > \text{C}(\text{CO}_2\text{Et})_2$ , m. p.  $82^\circ$ ; ethyl tetraethyl-diaminodiphenylmalonate, prisms, m. p.  $82.5^\circ$ ; the methyl ester, prisms, m. p.  $98^\circ$ ; methyl tetramethyldiaminodiphenylmalonate, leaflets, m. p.  $166^\circ$ ; methyl dimethylaminodiethylaminodiphenylmalonate,



needles, m. p.  $121^\circ$ . Alcoholic potassium hydroxide converts these esters into the corresponding tetra-alkyldiaminodiphenylacetic acids, which are unstable and have no definite m. p. (compare Weil, Abstr., 1894, i, 419). W. O. W.

*m*-Toluic Acid. ERICH MÜLLER (*Ber.*, 1909, 42, 423—434).—A continuation of the investigations of Findelee (Abstr., 1906, i, 42) and Jürgens (Abstr., 1907, i, 1036). The present communication deals principally with an improved method of converting *m*-toluic acid into 3-methylphthalic acid, and of various condensation products derived from the latter substance. Experiments have also been made with the object of definitely establishing the constitutions of the four possible nitro-*m*-toluic acids.

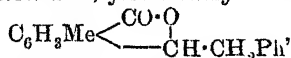
I. 3-Methylphthalic Acid.—3-Methylphthalic anhydride, when heated with phenylacetic acid in the presence of sodium acetate at  $236^\circ$ , yields benzylidene-3-methylphthalide,



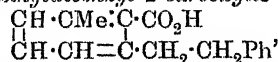
which crystallises in small leaflets, m. p.  $151^\circ$ , and is converted by a 10% aqueous solution of potassium hydroxide into 3-methyldeoxy-

benzoin-2-carboxylic acid,  $\begin{array}{c} \text{CH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ | \quad | \\ \text{CH} \cdot \text{CH} = \text{C} \cdot \text{CO} \cdot \text{CH}_2\text{Ph}' \end{array}$  crystallising with

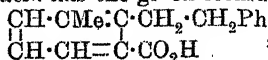
$1\text{H}_2\text{O}$  in gypsum-like crystals, m. p.  $77-79^\circ$ . The latter, when reduced with sodium amalgam, yields a salt of a  $\gamma$ -hydroxy-acid, which, when treated with hydrochloric acid, yields benzyl-3-methylphthalide,



which crystallises in groups of needles, m. p.  $87-92^\circ$ . If the salt of the  $\gamma$ -hydroxy-acid is heated at  $212^\circ$  for four hours, and then treated with dilute hydrochloric acid, it yields an oil which is undoubtedly 3-methylstilbene-2-carboxylic acid, for it is converted on reduction into 3-methyldibenzyl-2-carboxylic acid,



crystallising in nodular aggregates of rhombic prisms, m. p.  $125-126^\circ$ . It was shown that the acid has the given formula, and not



by V. Meyer's law of esterification (Abstr., 1895, i, 228; 1896, i, 547).

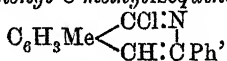
Although 3-methylphthalylglycine ethyl ester cannot be converted by Gabriel and Colman's method into an isoquinoline derivative

(compare Jürgens, *loc. cit.*), the latter may be obtained from 3-methylphthalic acid by the following method.

Benzylidene-3-methylphthalide is converted by gaseous nitrous acid into *nitrobenzylidene-3-methylphthalide*,  $C_6H_5Me \begin{smallmatrix} CO \cdot O \\ \diagdown \quad \diagup \\ CH : CPh \cdot NO_2 \end{smallmatrix}$ ,

which crystallises in yellow leaflets, m. p. 198—199° (decomp.), and is converted by hydriodic acid and red phosphorus into 3-phenyl-8-methylisocoumarin,  $C_6H_5Me \begin{smallmatrix} CO \cdot O \\ \diagdown \quad \diagup \\ CH : CPh \end{smallmatrix}$ , long, colourless needles, m. p. 131°.

The latter compound is converted by alcoholic ammonia into 3-phenyl-8-methylisocarbostyryl,  $C_6H_5Me \begin{smallmatrix} CO \cdot NH \\ \diagdown \quad \diagup \\ CH : CPh \end{smallmatrix}$ , which crystallises in small groups of needles, m. p. 231°, and is converted by boiling phosphoryl chloride into 1-chloro-3-phenyl-8-methylisoquinoline,



crystallising in needles, m. p. 64—65°. 3-Phenyl-8-methylisoquinoline,  $C_{16}H_{13}N$ , obtained by reducing the last-named compound with hydriodic acid and red phosphorus, has m. p. 51°; the *hydriodide*, pale yellow needles, m. p. 216—218° (decomp.); *hydrochloride*, long, slender needles, m. p. 236—240°; *chromate*, granular crystals, m. p. 164°; *platinichloride*, pale yellow needles, m. p. 221° (decomp.); *picrate*, granular crystals, m. p. 232°, and *aurichloride*,  $C_{16}H_{13}N \cdot HAuCl_4 \cdot H_2O$ , microscopic needles, m. p. 211° (decomp.), were prepared.

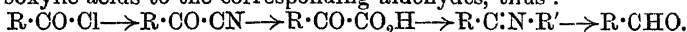
II. *Nitration of m-Toluic Acid*.—*m*-Toluic acid when nitrated is converted into 2-nitro-*m*-toluic acid, 4-nitro-*m*-toluic acid, and 6-nitro-*m*-toluic acid. It was shown that the compound, m. p. 215—216°, is 6-nitro-*m*-toluic acid by reducing it to the amino-compound and distilling the latter with lime, whereupon *o*-toluidine was obtained.

5-Amino-*m*-toluic acid,  $C_8H_9O_2N$ , crystallises in groups of small needles with a pink tint, m. p. 183°, and yields *m*-toluidine when distilled with lime.

*Methyl 6-nitro-m-toluate* has m. p. 81—82°; *methyl 5-nitro-m-toluate* crystallises in plates, m. p. 84—85°; *methyl 4-nitro-m-toluate* forms needles, m. p. 78—79°. W. H. G.

**Claisen's Acid Cyanide Synthesis.** FERDINAND MAUTHNER (*Ber.*, 1909, 42, 188—195).—It has been shown previously (*Abstr.*, 1908, i, 348) that 3:4:5-trimethoxybenzoyl cyanide may be prepared from 3:4:5-trimethoxybenzoyl chloride by Claisen's synthesis. In the present communication, it is shown that the chlorides of anisic acid, veratric acid, dimethylgentisic acid, 2:3:4-trimethoxybenzoic acid, and 3:4:5-trimethoxybenzoic acid may be converted by this method into the corresponding cyanides, which when hydrolysed are first converted into amides and finally into  $\alpha$ -ketocarboxylic acids. This method of preparation of the  $\alpha$ -keto-acids of phenol ethers is better than that devised by Bouveault (*Abstr.*, 1897, i, 530; 1898, i, 585; 1899, i, 286), because in this case the positions of the radicles in the molecule are known. By employing Bouveault's method of converting an  $\alpha$ -ketocarboxylic acid into the corresponding aldehyde

(Abstr., 1896, i, 649), it is possible to pass from phenol ether carboxylic acids to the corresponding aldehydes, thus :



*p*-Methoxybenzoyl cyanide,  $C_9H_7O_2N$ , prepared by the action of hydrogen cyanide on anisyl chloride in the presence of pyridine, crystallises in colourless needles, m. p. 63—64°. It is converted by cold concentrated hydrochloric acid into *p*-methoxyphenylglyoxylamide,  $C_9H_9O_3N$ , colourless needles, m. p. 151—152°, and *p*-methoxyphenylglyoxylic acid.

The following compounds are prepared by methods similar to those just described :

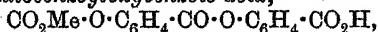
*m*-Methoxybenzoyl cyanide,  $C_9H_7O_2N$ , forms colourless crystals, m. p. 111—112°; it is not readily attacked by cold concentrated hydrochloric acid. 3:4-Dimethoxybenzoyl cyanide,  $C_{10}H_9O_3N$ , crystallises in colourless needles, m. p. 116—117°. 2:5-Dimethoxybenzoyl chloride,  $C_9H_9O_3Cl$ , prepared by the action of phosphorus pentachloride on 2:5-dimethoxybenzoic acid, is a colourless oil, b. p. 163—164°/15 mm. 2:5-Dimethoxybenzoyl cyanide,  $C_{10}H_9O_3N$ , forms pale yellow needles, m. p. 97—98°. 2:5-Dimethoxyphenylglyoxylamide,  $C_{10}H_{11}O_4N$ , crystallises in needles, m. p. 128—129°. The corresponding acid, first obtained by Bouveault as an oil, crystallises in needles, m. p. 75—76°. 2:3:4-Trimethoxybenzoyl chloride,  $C_{10}H_{12}O_4Cl$ , has b. p. 175—176°/11 mm., m. p. 42°. The corresponding cyanide,  $C_{11}H_{11}O_4N$ , crystallises in colourless needles, m. p. 89—90°. 2:3:4-Trimethoxyphenylglyoxylic acid,  $C_{11}H_{12}O_6$ , crystallises in colourless needles, m. p. 139—140°; the amide,  $C_{11}H_{13}O_5N$ , forms needles, m. p. 106—107°.

3:4:5-Trimethoxybenzoyl cyanide has b. p. 178—179°/14 mm.

W. H. G.

**Methyl-carbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetical Operations.** II. EMIL FISCHER (Ber., 1909, 42, 215—228).—The method of preparation of the chlorides of phenolcarboxylic acids described recently (Abstr., 1908, i, 892) cannot be employed with advantage when the hydroxyl group occupies a position ortho to the carboxyl group. *o*-Ethyl-carbonato-benzoic acid has been prepared, however, by Hofmann (Amer. Patent 1639, 174 of Dec. 12, 1899) by the action of ethyl chlorocarbonate on a mixture of salicylic acid and dimethylaniline in benzene. This method has now been employed to convert the two hydroxyl groups in 2:5-dihydroxybenzoic acid and 2:4-dihydroxybenzoic acid into methyl-carbonato-groups, and from the compounds formed the corresponding chlorides have been obtained. *o*-Coumaric acid, unlike salicylic acid, adds on the methyl-carbonato-group in an aqueous alkaline solution, and yields finally the chloride,  $CO_2Me \cdot O \cdot C_6H_4 \cdot CH : CH \cdot COCl$ .

*p*-Methyl-carbonatobenzoyloxybenzoic acid,



obtained by the action of *p*-methyl-carbonatobenzoyl chloride on *p*-hydroxybenzoic acid, crystallises in very small, slender needles, m. p. 216—217° (corr., decomp.); it is converted by dilute aqueous ammonia into *p*-hydroxybenzoyloxybenzoic acid, m. p. about 270° (decomp.): Klepl gives m. p. 261° (Abstr., 1884, 446).

*o*-Methyl-carbonatobenzoic acid,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , forms long, glistening plates, m. p.  $135^\circ$  (corr., decomp.); it is converted by phosphorus pentachloride into *o*-methyl-carbonatobenzoyl chloride,  $\text{C}_6\text{H}_4\text{O}_2\text{Cl}$ , a colourless liquid, b. p.  $107\text{--}110^\circ/0.1\text{ mm.}$ ; the latter compound reacts with glycine or glycine ester, forming methyl-carbonatosalicylic acid, a viscid oil which is hydrolysed by aqueous sodium hydroxide, yielding salicylic acid (compare Bondi, Abstr., 1907, i, 766). A substance,  $\text{C}_{10}\text{H}_7\text{O}_5\text{N}$ , is obtained as an intermediate product in the condensation of the chloride with glycine; it crystallises in very thin, glistening, microscopic plates, m. p.  $228^\circ$  (corr.).

5-Methyl-carbonato-2-hydroxybenzoic acid,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{H}$ , obtained by the action of methyl chlorocarbonate on gentisic acid dissolved in *N*-sodium hydroxide solution, crystallises in long, colourless needles, m. p.  $171^\circ$  (corr.); it is converted by methyl chlorocarbonate and dimethylaniline in benzene into 2:5-dimethyl-carbonatobenzoic acid,  $(\text{CO}_2\text{Me}\cdot\text{O})_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ , crystallising in thin plates, m. p.  $144\text{--}145^\circ$  (corr., decomp.); the chloride,  $\text{C}_{11}\text{H}_9\text{O}_7\text{Cl}$ , forms microscopic needles, m. p.  $119^\circ$  (corr.).

4-Methyl-carbonato-2-hydroxybenzoic acid,  $\text{C}_9\text{H}_8\text{O}_6$ , crystallises in long needles, m. p.  $143^\circ$  (corr.). 2:4-Dimethyl-carbonatobenzoic acid,  $\text{C}_{11}\text{H}_{10}\text{O}_6$ , forms long needles, m. p.  $159^\circ$  (corr., decomp.); the corresponding chloride,  $\text{C}_{11}\text{H}_9\text{O}_7\text{Cl}$ , crystallises in slender needles or thin leaflets, m. p.  $86\text{--}87^\circ$  (corr.).

*o*-Methyl-carbonatocinnamic acid,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , crystallises in slender needles, m. p.  $185^\circ$  (corr.); the chloride,  $\text{C}_{11}\text{H}_9\text{O}_4\text{Cl}$ , forms slender, pliable needles. W. H. G.

### Condensation of Aldehydes with Phenolcarboxylic Acids.

II. E. HÖST MADSEN (*Arch. Pharm.*, 1909, 247, 65—77).—An extension of the reaction described previously (Abstr., 1907, i, 423) to other aromatic aldehydes and acids.

4:4'-Dihydroxy-5:5'-dimethyltriphenylmethane-3:3'-dicarboxylic acid, m. p.  $248^\circ$  (approx., decomp.), obtained from benzaldehyde and *o*-cresotic acid by the general process (*loc. cit.*), crystallises with  $1\text{H}_2\text{O}$  from ether on addition of light petroleum in tufts of colourless needles, and gives in alcoholic solution on addition of ferric chloride a bluish-violet coloration. The diacetyl derivative, m. p.  $140\text{--}145^\circ$ , separates from dilute alcohol in colourless crystals with  $1\text{H}_2\text{O}$ , and gives no colour immediately with ferric chloride, but yields a bluish-violet colour with this reagent after boiling with water for some minutes.

4:4'-Dihydroxy-6:6'-dimethyltriphenylmethane-3:3'-dicarboxylic acid, m. p.  $271^\circ$  (approx., decomp.), obtained by condensing benzaldehyde with *m*-cresotic acid, crystallises from dilute alcohol in colourless, felted needles, and is similar in solubility to the first isomeride described, but gives a redder coloration with ferric chloride. The diacetyl derivative, m. p.  $240\text{--}245^\circ$  (decomp.), crystallises in colourless needles or rhomboidal plates, and gives a violet coloration with ferric chloride after boiling with water.

2:2'-Dihydroxy-5:5'-dimethyltriphenylmethane-3:3'-dicarboxylic acid, m. p.  $240^\circ$  (approx., decomp.), obtained from benzaldehyde and

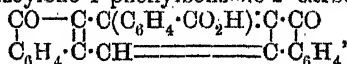
*p*-cresotic acid, forms a colourless, crystalline powder, and generally resembles the two isomerides described above, but is somewhat hygroscopic. The *diacetyl* derivative, m. p. 135—140°, crystallises in thin plates, and, unlike the two isomerides described above, is soluble in chloroform, ether, or hot water.

When vanillin is heated with salicylic acid in presence of hydrochloric acid by the general process, no condensation to a triphenylmethane derivative occurs, but decomposition ensues and phenols are formed. *Vanillin salicylate*, m. p. 110° (approx.), is obtained when phosphoric oxide is added to salicylic acid and vanillin dissolved in ether, and the mixture heated under a reflux apparatus during twenty-four hours. It is coloured green by ammonia, gives a violet coloration with Millon's reagent, and yields the characteristic colour reaction of salicylic acid with ferric chloride after boiling in water during a few minutes. The *oxime*, m. p. 164·5°, of the ester forms long, colourless needles.

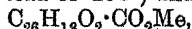
No condensation products could be obtained by the general process with (1) paraldehyde and *o*-cresotic acid, (2) acetone and *o*-cresotic acid, or (3) benzaldehyde and *o*-resorcylic acid. T. A. H.

**Derivatives of Phenenytribenzoic [1:3:5-Triphenylbenzene-2':2'':2'''-tricarboxylic] Acid.** GIORGIO ERRERA and A. VACCARINO (*Gazzetta*, 1909, 39, i, 1—11).—The authors have investigated further the two isomeric acids obtained by the action of concentrated sulphuric acid on phenenytribenzoic acid (compare Errera, *Abstr.*, 1908, i, 185), which are found to have m. p. 362° (instead of 349—350°) and 335—336° (instead of 321°) respectively. The quantities of the two acids obtained are always very nearly in the ratio 4 (m. p. 362°):1 (m. p. 335—336°), no matter whether the phenenytribenzoic acid is used in the crude form or after repeated crystallisation. Both are transformed slowly, but completely, into tribenzoylenebenzene under the prolonged action of concentrated sulphuric acid on the water-bath. Both acids are also esterified moderately readily by Fischer's method, the one with the lower m. p. rather more slowly than the other, probably owing to its less solubility. The observation that tribenzoylenebenzene is formed the more readily from the acid, m. p. 335—336°, leads the authors to interchange the two structural formulæ previously given (*loc. cit.*).

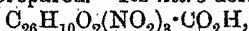
2:3:5:6-Dibenzoylene-1-phenylbenzene-2'-carboxylic acid,



has, therefore, m. p. 362°. Its *sodium* salt,  $\text{C}_{27}\text{H}_{15}\text{O}_4\text{Na}\cdot\text{H}_2\text{O}$ , and its ethyl ester (m. p. 260°, instead of 253°) and *methyl* ester,

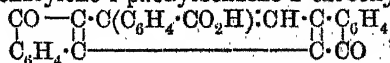


m. p. 336—337°, were prepared. Its *nitro*-derivative,



is deposited from nitrobenzene in yellow needles or large, brick-red crystals, m. p. about 429°.

3:4:5:6-Dibenzoylene-1-phenylbenzene-2-carboxylic acid,



crystallises from alcohol in pale yellow, silky needles, m. p. 335—336°. Its *ethyl* ester,  $C_{26}H_{18}O_2 \cdot CO_2Et$ , crystallises from light petroleum in elongated, yellow laminæ, m. p. 226°, and its *methyl* ester,  $C_{26}H_{18}O_2 \cdot CO_2Me$ , crystallises from light petroleum in minute, yellow laminæ, m. p. 248—249°; the *sodium* salt,  $C_{27}H_{18}O_4Na \cdot 5H_2O$ , was prepared.

Triethyl phenenyltribenzoate (compare Abstr., 1908, i, 185) separates from light petroleum in faintly yellow, prismatic crystals, m. p. 71°, belonging to the monoclinic system [FRANCESCO RANFALDI:  $a:b:c = 0.48681:1:0.95873$ ;  $\beta = 88^\circ 31' 24''$ ].

Trimethyl phenenyltribenzoate,  $C_6H_5(C_6H_4 \cdot CO_2Me)_3$ , separates from methyl alcohol as a mass of colourless crystals, m. p. 94—95°.

The great differences between these esters of phenenyltribenzoic acid and the corresponding ones of phenylnaphthalenedicarboxylic acid (Lanser's "diphenyltetrenedicarboxylic acid") (compare Michael, Abstr., 1906, i, 518; Lanser, Abstr., 1899, i, 916) afford a further confirmation of Michael's views that these two acids are distinct.

T. H. P.

**Inosic Acid.** PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 335—338).—The authors furnish additional evidence of the constitution previously suggested for inosic acid (Abstr., 1908, i, 931). By heating a 2½% aqueous solution of the barium salt for six hours at 125—130° in a sealed tube, barium phosphate is eliminated, and from the solution, which does not contain a pentose or hypoxanthine, Hauser and Wenzel's inosine (Abstr., 1908, i, 561) has been isolated; by more prolonged heating of the barium salt, carnine itself is formed.

Hauser and Wenzel regard inosic acid and carnine as being derived from the same parent substance. The authors believe that carnine is a degradation product of inosic acid.

C. S.

**Preparation of Aldehydes and Acid Anhydrides.** AUGUSTE BÉHAL (*Compt. rend.*, 1909, 148, 179—182. Compare this vol., i, 145).—Benzaldehyde can be prepared by boiling for thirty-two hours a mixture of benzylidene chloride (1 mol.) and acetic acid (2 mols.). Catalysts, such as cobalt chloride, facilitate the reaction, which is probably expressed by the equation:  $CHPhCl_2 + 2HOAc = Ph \cdot CHO + Ac_2O + 2HCl$ . The formation of acetyl chloride, which occurs when only 1 mol. of acetic acid is employed, is probably due to the action of hydrogen chloride on the acetic anhydride.

Curves are given showing the rate of evolution of hydrogen chloride when varying amounts of acetic acid are employed. This reaction is stated to be general.

W. O. W.

**Asymmetric Synthesis.** PAUL FREUNDLER (*Ber.*, 1909, 42, 233—234. Compare Henle and Haack, this vol., i, 6).—It was desired to carry out a reaction, which requires the influence of light, with a racemic compound in circularly polarised light. To this end the conversion of *r-o*-nitrobenzaldehydediamylacetal (b. p. 186—187°/11 mm.), dissolved in *r*-amyl alcohol, into amyl *o*-nitrosobenzoate was studied. The Heraeus quartz mercury lamp was used as the source of light, and screened so that the light was mainly  $\lambda = 398$ . Action

was continued for 400 hours, but in a single experiment no evidence of optical activity could be detected. E. F. A.

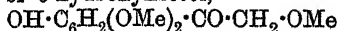
**Constitution of "Dichloropiperonal."** HERMANN PAULY (*Ber.*, 1909, 42, 417—422. Compare *Abstr.*, 1907, i, 709).—Dichloropiperonal, formed by the action of sulphur chloride or sulphur dichloride on piperonaldehyde, could not be isolated in a pure state, hitherto, owing to the presence of colloidal sulphur (compare Schimmel & Co., *Abstr.*, 1906, i, 513). It is now found that the sulphur can be removed by passing a current of chlorine into the mixture and distilling off the sulphur dichloride under reduced pressure; pure dichloropiperonal is obtained by crystallising the residue from chloroform. Since it is so readily prepared by this method, it seemed highly probable that dichloropiperonal had the formula originally given to it by Fittig and Remsen, namely,  $\text{COH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{CCl}_2$ ;

nevertheless, it has been found that when this substance is reduced with zinc dust, it does not regenerate piperonaldehyde, but yields methylcatechol carbonate; thus proving the correctness of Delange's view that dichloropiperonal is really dichloromethylcatechol carbonate (*Abstr.*, 1907, i, 700).

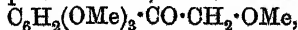
*Methylcatechol carbonate*,  $\text{C}_8\text{H}_8\text{O}_3$ , has m. p. 34—35°, b. p. 133—135.5°/26 mm., 238—241°/760 mm. It is converted by 50% aqueous pyridine into homocatechol (3:4-dihydroxytoluene), which has m. p. 65° (corr.) and b. p. 251° (corr.). Béhal and Desvignes give m. p. 51° (*Abstr.*, 1892, 1312). W. H. G.

**Crystalline Form of 3:4'-Dimethylbenzophenone.** PAUL P. SCHORIGIN (*Bull. Acad. Sci. St. Petersburg*, 1909, 79—80. Compare *Ber.*, 1903, 36, 2027).—This ketone crystallises readily from alcohol in the form of long, monoclinic needles [ $a:b:c = 1.0409:1:0.4154$ ,  $\beta = 91^\circ 45'$ ], m. p. 82°, b. p. 328—330°/760 mm.,  $D_4^{20} 1.134$ . Z. K.

**Completely Methylated Flavone Derivatives.** JOSEF HERZIG and BR. HOFMANN (*Ber.*, 1909, 42, 155—159. Compare *Abstr.*, 1891, 1386; 1893, i, 413).—Morin reacts with methyl sulphate in the presence of a large excess of sodium hydroxide solution, yielding the *pentamethyl ether*,  $\text{C}_{15}\text{H}_8\text{O}_2(\text{OMe})_5$ , which crystallises from alcohol in colourless needles m. p. 154—157°. Its alcoholic solution is colourless, but turns yellow on the addition of potassium hydroxide solution. When boiled with alcoholic potash, it yields 2:4-dimethoxybenzoic acid and the *trimethyl ether of o-hydroxyfisetol*,



(6-hydroxy-2:4-dimethoxyphenyl methoxymethyl ketone), which separates from alcohol in compact, colourless crystals, m. p. 102—104°. The *oxime*,  $\text{C}_8\text{H}_8\text{O}_2\text{N}(\text{OMe})_3$ , crystallises from dilute methyl alcohol in colourless needles, m. p. 147—149°, and the *methyl ether*,

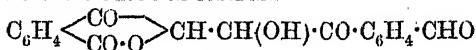


has m. p. 49—52°.

A 25% yield of quercetin pentamethyl ether (Waliaschko, *Abstr.*, 1904, i, 760) can be obtained by treating quercetin with methyl

sulphate and sodium hydroxide and keeping for several days. When warmed with alcoholic potash, the ether yields 3:4-dimethoxybenzoic acid and the trimethyl ether of *o*-hydroxyfisetol. J. J. S.

**Bisdiketohydrindene.** HUGO VOSWINCKEL (*Ber.*, 1909, 42, 465—470).—Considerable amounts of Nathanson's bisdiketohydrindene (diphthalylethane) (*Abstr.*, 1894, i, 38) are obtained in the preparation of dihydroxynaphthacenequinone (Gabriel and Leupold, *Abstr.*, 1898, i, 482). When treated with a mixture of glacial acetic and nitric acid (1.48) at 0°, the hydrindene derivative yields a mixture of two oxidation products. The one dissolves readily in cold benzene, whereas the other is very sparingly soluble. This second compound,  $C_{18}H_{12}O_6$ , crystallises from hot chloroform in short, six-sided prisms, m. p. 211°, and the structural formula

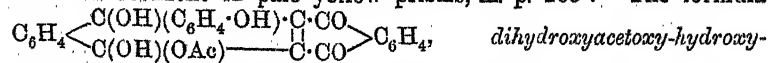


is suggested. It yields an *acetyl* derivative,  $C_{20}H_{14}O_7$ , m. p. 315°, a *benzoyl* derivative,  $C_{25}H_{16}O_7$ , m. p. 268°, and a *methyl* ether,  $C_{19}H_{14}O_6$ , which turns brown at 240° and decomposes at higher temperatures. With phenylhydrazine the oxidation product yields a complex condensation product,  $(C_{18}H_{12}O_6 + 5C_6H_5N_2 - 5H_2O)$ , which crystallises from glacial acetic acid in red needles with a high metallic lustre and m. p. 209°.

The oxidation product dissolves in cold normal sodium hydroxide solution, and the immediate addition of hydrochloric acid yields an *acid*,  $C_{18}H_{12}O_6 \cdot 2H_2O$ , which crystallises from glacial acetic acid in clear prisms, m. p. 240°. Its solutions in ammonia or alkali carbonates have a reddish-brown colour, and those in alkali hydroxides a reddish-brown colour which changes rapidly to blue.

Hot sodium hydroxide transforms the oxidation product into *phthalonaldehydic acid*,  $COH \cdot C_6H_4 \cdot CO \cdot CO_2H$ , which crystallises from water in small prisms and plates, m. p. 144°. Its *phenylhydrazone* has m. p. 229°. J. J. S.

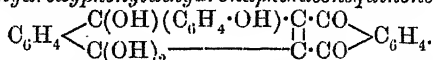
**The Naphthacene Series. II.** HUGO VOSWINCKEL (*Ber.*, 1909, 42, 458—465. Compare *Abstr.*, 1906, i, 99).—Phenol and acetic acid react with naphthacenediquinone in the presence of sulphuric acid, yielding a product,  $C_{18}H_8O_4 \cdot C_6H_5O \cdot C_2H_4O_2$ , which crystallises from nitrobenzene in pale yellow prisms, m. p. 285°. The formula



*phenyldihydronaphthacenequinone* is suggested. The phenolic group is firmly attached, and cannot be removed by reduction or hydrolysis, whereas the acetyl group is readily eliminated. Acetic anhydride and zinc chloride transform the condensation product into the *tetra-acetyl* derivative,  $C_6H_4 \begin{array}{c} \diagup C(OAc)(C_6H_4 \cdot OAc) \cdot C \cdot CO \diagdown \\ \diagdown C(OAc)_2 \text{---} C \cdot CO \diagup \end{array} C_6H_4$ , which forms pale yellow crystals, m. p. 283°.

The condensation product dissolves in dilute alkalis, yielding brownish-violet-coloured solutions, and the addition of mineral acids yields the three products :

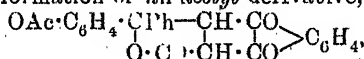
1. *Trihydroxy-phenyldihydronaphthacenequinone*,



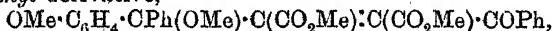
—It is insoluble in benzene, but crystallises from dilute alcohol in yellow prisms, m. p. 190°, dissolves in alkalis, giving characteristic colorations, and dyes silk an orange colour. Its solution in concentrated sulphuric acid has a reddish-violet colour, which turns to a steel-blue when warmed; with acetic anhydride and zinc chloride it yields a *monoacetyl* derivative,  $\text{C}_{26}\text{H}_{18}\text{O}_7$ , which separates from glacial acetic acid as a colourless, crystalline powder, m. p. 285°.

2. An acid,  $\text{C}_6\text{H}_5\cdot\text{C(OH)(C}_6\text{H}_4\cdot\text{OH)}\cdot\text{CH}\text{---}\text{CO} \begin{array}{c} \text{CO}_2\text{H}\cdot\text{C}\cdot\text{C(OH)}_2 \end{array} \text{C}_6\text{H}_4$ , which can be

isolated as the calcium salt. The acid separates as a flocculent mass containing water of crystallisation; when heated at 80°, it loses  $0\cdot5\text{H}_2\text{O}$ , assumes a crystalline texture, and then melts at 130°. Treatment with acetic anhydride and zinc chloride leads to the elimination of water and the formation of an *acetyl* derivative,



which crystallises from glacial acetic acid in golden-yellow plates, m. p. 266°. Treatment with methyl sulphate transforms the acid into a *tetramethyl* derivative,



which forms colourless plates, m. p. 124°.

3. A compound,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C(C}_6\text{H}_4\cdot\text{OH)(OH)}\cdot\text{CH}\cdot\text{C(OH)} \\ \text{CO} \text{---} \text{CH}\cdot\text{C(OH)} \end{array} \text{C}_6\text{H}_4$  (?),

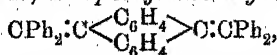
which crystallises from dilute alcohol in orange-coloured needles, m. p. 174°. It dissolves in alkali hydroxides to a violet solution, and in sulphuric acid to a pure blue solution. It yields a *monoacetyl* derivative,  $\text{C}_{26}\text{H}_{18}\text{O}_6$ , m. p. 172°.

Resorcinol, orcinol, and phloroglucinol condense with naphthacenediquinone and glacial acetic acid in the absence of sulphuric acid. The product obtained from resorcinol has the composition  $\text{C}_{24}\text{H}_{14}\text{O}_6$ , and forms a reddish-brown, crystalline powder, m. p. 234°.

*Naphthacenequinohydron*,  $\text{C}_{18}\text{H}_8\text{O}_4$ ,  $\text{C}_{18}\text{H}_{10}\text{O}_4$ , is obtained by the union of naphthacenediquinone with dihydronaphthacenequinone in nitrobenzene solution, and is identical with the compound previously described as a desmotropic modification of naphthacenediquinone.

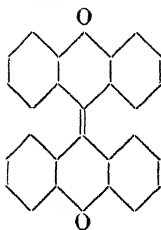
J. J. S.

**Reactions of 9:10-Dihydroanthracene and of Anthranol.**  
ROBERT PADOVA (*Compt. rend.*, 1909, 148, 290—292).—When 9:10-dihydroanthracene is heated at 250° for two and a-half hours with diphenyldichloromethane, *tetraphenylanthracenylidene*,

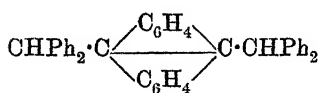


is obtained. This has m. p. 305°, and is identical with the substance

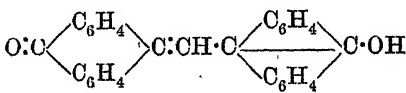
obtained by Staudinger (Abstr., 1908, i, 410) by the action of anthraquinone on diphenylketenquinoline. On reduction with sodium and benzyl alcohol, it yields the compound I (below), which has m. p. above  $360^{\circ}$  and shows an intense violet fluorescence.



Dianthraquinone (annexed formula) is said to be formed by the action of amyl nitrite on a solution of dianthrone in pyridine. The action of chloroform and alcoholic potassium hydroxide on anthranol leads to the formation of a substance crystallising in deep red prisms, m. p. above  $310^{\circ}$ . This is 10-oxanthryl-9-anthraquinonementhane (formula II). The *acetyl* derivative has m. p.  $201-202^{\circ}$ . The *benzoyl* derivative forms canary-yellow prisms, m. p.  $216-218^{\circ}$ .



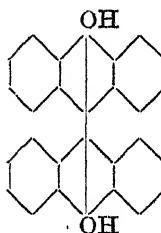
(I.)



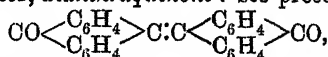
(II.)

W. O. W.

**New Reduction Product of Anthraquinone.** HANS MEYER (*Ber.*, 1909, 42, 143—145).—When anthraquinone is reduced with zinc dust and alkali at high temperatures and under pressure, the product is the enolic form of *dianthranol* (annexed formula) (compare Dimroth, Abstr., 1901, i, 198). It is extremely stable, and appears to exist in two forms, of which one is obtained in dark brown, glistening crystals, whilst the other is pale yellow. The m. p. is about  $230^{\circ}$ , but is not sharp. The name dianthranol is assigned to this compound, that previously described as dianthranol or dianthrone (*loc. cit.*) being regarded as the ketonic form and therefore termed dianthrone. Its solutions in aqueous alkali hydroxides are reddish-yellow. The *diacetyl* derivative forms yellow needles, m. p.  $273^{\circ}$ ; the *dimethyl ether* has m. p.  $245^{\circ}$ . Both yield dihydroanthracene when reduced with hydriodic acid, and anthraquinone when oxidised with chromic acid.



Feeble oxidising agents, ferric chloride, alkaline permanganate, or a solution of iodine in potassium iodide solution, transform the phenol into *bianthrone* [better, *dianthraquinone*: see preceding abstract],



a lemon-yellow compound which is stable and sparingly soluble in most solvents. Its solutions at high temperatures have a green colour, and it is also turned green by pressure.

Prolonged heating with an alcoholic solution of hydrogen chloride transforms dianthranol into dianthrone, and alcoholic potassium hydroxide brings about the reverse change.

J. J. S.

**Action of Magnesium on a Mixture of Allyl Bromide and a Terpene Ketone.** W. JAVORSKY (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1746—1748).—The author has prepared the following alcohols by

the action of magnesium on a mixture of allyl bromide and a ketonic compound under the conditions previously laid down (Abstr., 1908, i, 753).

3-Allylmenthan-3-ol,  $C_{13}H_{24}O$ , b. p.  $130^{\circ}/22$  mm., prepared from allyl bromide and menthone.

2-Allylborneol, b. p.  $130^{\circ}/20$  mm., from camphor and allyl bromide.

$\Delta^4$ -Allyl-3-p-menthen-3-ol,  $C_{13}H_{22}O$ , b. p.  $135^{\circ}/27$  mm., from pulegone and allyl bromide.

These three alcohols, which were obtained in about 90% yields, are colourless, mobile liquids.

Treated under the above conditions with allyl bromide, piperonal yields a thick, yellow liquid, b. p.  $169-170^{\circ}/27$  mm.; furfuraldehyde, a thick, yellow liquid, b. p.  $266-272^{\circ}$ ; menthyl oxide, a colourless, mobile liquid, b. p.  $168-170^{\circ}$  (slight decomp.), with a smell like that of camphor; benzylideneacetone, an almost colourless liquid, b. p.  $165^{\circ}$ , at which temperature water is given off; benzil, a thick brown liquid, which decomposes when distilled under 22 mm. pressure. These products are under investigation.

The reaction between allyl bromide and a ketonic compound in presence of magnesium sometimes fails without apparent reason. One condition necessary for success is a slow, gentle action, any strong heating always lowering the yield of alcohol.

T. H. P.

**The Grignard Synthesis. Action of Magnesium Phenyl Bromide on Camphor.** H. JERMAIN M. CREIGHTON (*Trans. Nova Scotia Inst. Sci.*, 1908, 11, (4), 593-597).—The interaction of ethereal magnesium phenyl bromide and camphor in equal molecular quantities at  $60^{\circ}$  leads to the formation of *phenylborneol*,  $C_{10}H_{16}Ph\cdot OH$ , b. p.  $258-260^{\circ}$  or  $143-145^{\circ}/14$  mm.,  $D_{20} 0.977$ ,  $[\alpha]_D^{25} 7^{\circ}55'$ , in alcoholic solution (compare Zelinsky, Abstr., 1901, i, 660). C. S.

**Attempts to Resolve Racemic Camphoric Acid and isoborneol into Active Components.** ERNST BECKMANN (*Ber.*, 1909, 42, 485-491. Compare Pickard and Littlebury, *Trans.*, 1907, 91, 1973).—The *isoborneol* obtained from camphene by Bertram and Walbaum's method (Abstr., 1894, i, 204) has m. p.  $212^{\circ}$ , and is slightly dextrorotatory in solution, the value for  $[\alpha]_D$  varying from  $+1.2^{\circ}$  to  $+3.9^{\circ}$  according to the solvent used. When oxidised, the *isoborneol* yields a camphor which is slightly levorotatory, and on further oxidation a camphoric acid, which is also slightly levorotatory. No *isocamphoric acid* is formed, as treatment with acetyl chloride completely transforms the acid into its anhydride.

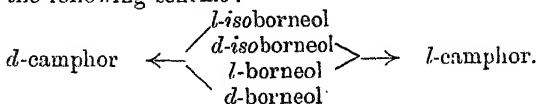
The acid obtained is mainly *r*-camphoric acid, with a slight excess of the *l*-acid, and can be resolved by repeatedly crystallising the acid cinchonidine salt from aqueous alcohol. The *d*-acid had m. p.  $183^{\circ}$  and  $[\alpha]_D +44.4^{\circ}$ , and the *l*-acid, m. p.  $186-187^{\circ}$  and  $[\alpha]_D -50.7^{\circ}$ .

Attempts to resolve the *isoborneol* itself were made by conversion into the *isobornyl* hydrogen succinate, and resolution of this by means of its cinchonidine salt.

*isobornyl* succinate,  $C_{24}H_{38}O_4$ , has m. p.  $37^{\circ}$ , and resembles camphor in appearance. *isobornyl* hydrogen succinate,  $C_{14}H_{22}O_4$ , is a clear oil with an acid taste and an odour of *isoborneol*. The cinchonidine salt,

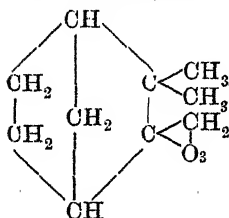
$C_{23}H_{14}O_5N_2$ , crystallises from dilute alcohol in slender needles, m. p.  $107^\circ$ . By crystallising from its 40% alcoholic solution, nine fractions, with  $[a]_D$  varying from  $+11.3^\circ$  to  $-2.5^\circ$ , were obtained.

The genetic relationship of the camphors and borneols is represented by the following scheme:



J. J. S.

**Components of Ethereal Oils. Constitution of Camphene.** Its Oxidation with Ozone. FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 246—252).—When ozonised, camphene forms only one ozonide, which is decomposed in two ways: on the one hand (to the extent of about 30%) into camphenilone,  $C_9H_{14}O$ , and this to a hydroxy-acid,  $\delta$ -hydroxycamphenilonic acid, which forms a beautifully crystalline  $\delta$ -lactone,  $C_9H_{14}O_2$ , whilst, on the other hand, acids,  $C_9H_{14}O_2$ , are formed.



Camphene ozonide, annexed formula, prepared by leading a stream of ozone through camphene dissolved in chloroform, is a viscid oil, which decomposes when distilled in a vacuum. Cam-

phenilone,  $CH \begin{array}{c} \swarrow \text{CH}_2 \cdot \text{CH}_2 \\ \searrow \text{CH}_2 \\ \swarrow \text{CMe}_2 \cdot \text{CO} \end{array} CH$ , has m. p.

$40^\circ$ ,  $D^{20}_D$  0.9705. The semicarbazone,  $C_9H_{14} \cdot N \cdot NH \cdot CO \cdot NH_2$ , has m. p.  $223^\circ$ ; the oxime has m. p.  $109^\circ$ , b. p.  $128-129^\circ/14$  mm. The nitrile,  $C_9H_{13}N$ , prepared by boiling the oxime with dilute sulphuric acid, has b. p.  $85-90^\circ/12$  mm.,  $D^{20}_D$  0.9449,  $n_D$  1.47348. Camphocenic acid, obtained by the action of alcoholic potassium hydroxide on the nitrile, has b. p.  $145-146^\circ/11$  mm.,  $D^{20}_D$  1.020,  $n_D$  1.4862.

$\delta$ -Hydroxycamphenilonic acid,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{CMe}_2 \cdot \text{OH}) \\ \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \end{array} \begin{array}{c} \swarrow \\ \searrow \end{array} CH_2$ , forms a thin syrup, b. p.  $125-175^\circ/10$  mm., which decomposes, forming a solid distillate of the lactone. This has m. p.  $95-96^\circ$ , b. p.  $126-128^\circ/10$  mm., and forms large plates; it dissolves slowly in a slight excess of potassium hydroxide, and this solution yields a colourless silver salt. The silver salt interacts with methyl iodide, forming methyl  $\delta$ -hydroxycamphenilionate, b. p.  $126-127^\circ/10$  mm.,  $D^{20}_D$  1.0423,  $n_D$  1.46757. Both the acid and lactone behave as saturated compounds to permanganate. The acid,  $C_9H_{14}O_3$ , obtained also by the decomposition of camphene ozonide in a vacuum, is regarded as a mixture of an unsaturated monocyclic and a saturated bicyclic acid. It has b. p.  $136-140^\circ/10$  mm.,  $D^{20}_D$  1.028,  $n_D$  1.475; the methyl ester has b. p.  $94-96^\circ/10$  mm.,  $D^{20}_D$  0.988,  $n_D$  1.46261.

In view of these results, crude camphene consists to the greater part of semi-cyclic-camphene,  $CH \begin{array}{c} \swarrow \text{CH}_2 \text{---} \text{CH}_2 \\ \searrow \text{CH}_2 \\ \swarrow \text{CMe}_2 \cdot \text{C}(\text{CH}_3) \end{array} CH$ .

E. F. A.

Constituents of Ethereal Oils. Inversion of Carvenene,  $C_{10}H_{16}$  (Terpinene?), into *iso*Carvenene,  $C_{10}H_{16}$  (*iso*Terpinene?). FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 522—527. Compare this vol., i, 110).—Carvenene has the following constants:  $D^{20}_D$  0.8443,  $n^{20}_D$  1.49065, which result confirms the conclusion previously arrived at that cyclic conjugated double linkings cause an exaltation in the molecular refraction (cal. 45.240, found 46.619). When carvenene is heated with alcoholic sulphuric acid for two hours, *isocarvenene*,  $C_{10}H_{16}$ , b. p. 59—62°/10 mm.,  $D^{20}_D$  0.845,  $n_D$  1.480 (the exaltation in this case is only 0.4), and a *dicarvenene*,  $C_{20}H_{32}$ , b. p. 170—173°/10 mm.,  $D^{20}_D$  0.928,  $n_D$  1.5175, are obtained. The physical constants for *isocarvenene* are identical with those of terpinene obtained from sabinene mono- or di-hydrochloride, and it has been found that all terpinenes are converted into a terpene by alcoholic sulphuric acid, the physical data of which agree with those of *isocarvenene*. This compound yields terpinene nitrosite identical with that obtained from carvenene. In order to investigate further the conversion of carvenene into the *iso*-compound, the action of bromine on "terpinene" from sabinene dihydrochloride in amyl alcohol-ether solution was studied; crystals of terpinol tetrabromide were deposited, thus proving that terpinol is present in the "terpinene," which has hitherto been regarded as pure when prepared from the dihydrochloride.

Carvenene, on repeated reduction with sodium and amyl alcohol, gives *dihydrocarvenene* ( $\Delta^2$ -*tetrahydrocymene*),  $C_{10}H_{18}$ , an oil, b. p. 55—56°/12 mm.,  $D^{20}_D$  0.824,  $n_D$  1.461. Oxidation of carvenene with ozone yields dimethylacetylacetone (b. p. 82—86°/10 mm.).

Carvenene is regarded as  $\Delta^{1:3}$ -dihydrocymene, and *isocarvenene*,  $\Delta^{1:4}$ -dihydrocymene. W. R.

Sesquiterpenes. ERNST DEUSSEN (*Ber.*, 1909, 42, 376—381; 680).

—The author is unable to say from which of the two, and possibly three, isomeric hydrocarbons present in caryophyllene (*Abstr.*, 1908, i, 353) the following substances are derived.

The oxidation of caryophyllene ( $\alpha$  -14°) by dilute aqueous potassium permanganate at 0° yields a glycol,  $C_{15}H_{22}O_4$ , m. p. 120.5° (*loc. cit.*); from the oily potassium salts remaining after the removal of the glycol, two acids have been obtained. One is a liquid monobasic acid,  $C_{10}H_{16}O_3$ , which forms a crystalline *semicarbazone*,  $C_{11}H_{19}O_3N_3$ , m. p. 186° (slight yellow coloration), and the other is a crystalline monobasic acid,  $C_8H_8O_4$ , m. p. 179.5—180.5°, which sublimes without decomposition, does not form a semicarbazone, and is not identical with Baeyer's  $\Delta^{2:4}$ -dihydrophthalic acid.

When a solution of caryophyllene in acetone containing a little water is cooled in a freezing mixture and oxidised by the gradual addition of powdered potassium permanganate (two atomic proportions of oxygen), a substance,  $C_{10}H_{16}O_3$ , m. p. 145—146°, is obtained, which separates from hot benzene in white needles, is unchanged by dilute sodium hydroxide at 100°, has a bitter-sweet taste, and

appears to be a glycol, since it is changed by dilute sulphuric acid to an amorphous, white substance,  $C_{10}H_{16}O_2$ .

[With A. LOESCHE.]—The residue remaining after the distillation in a vacuum of oil of clove stalks freed from eugenol, yields by treatment with alcohol a voluminous, white substance,  $(C_{21}H_{30}O)_5$ , m. p.  $146^\circ$ , which can be purified by repeated precipitation of its chloroform solution by alcohol. C. S.

**Ethereal Oil of the Root Bark of *Cinnamomum zeylanicum*.** A. A. L. PILGRIM (*Pharm. Weekblad*, 1909, 46, 50—54).—The chief constituent of the oil of the root bark of *Cinnamomum zeylanicum* is camphor. The other constituents are pinene, cineol, dipentene, phellandrene, eugenol, safrole, probably carophyllene and borneol, and possibly cinnamaldehyde. The oil from the leaves contains 76% of eugenol along with pinene and cinnamaldehyde. The oil from an old sample of the stem bark contained 50% of cinnamaldehyde, and that from a specimen of young bark, 70—75%. In both, pinene, benzaldehyde, and eugenol were also present. A. J. W.

**Extracts containing Glucosides.** LEOPOLD ROSENTHALER and R. MEYER (*Arch. Pharm.*, 1909, 247, 28—49).—The object of this research was to determine whether in the preparation of extracts of drugs containing glucosides by exhaustion with water, as recommended by various Pharmacopeias, decomposition of the glucosides ensued, and, if so, whether this could be prevented by (1) neutralising the natural acids of the drug by adding calcium carbonate, and (2) by rendering the enzymes inactive by immersing the drug in boiling 95% alcohol.

Experiments with gentian, centaury, alder bark, cascara sagrada bark, and rhubarb showed that the first question must be answered in the affirmative, that although in none of these cases did the calcium carbonate exert any deleterious action, its protective action with respect to the glucosides was slight, and that extraction with hot alcohol is harmful in the case of centaury, is of no advantage in the case of alder bark, but is to be recommended in the cases of gentian, cascara sagrada bark, and rhubarb. The methods adopted in estimating the glucosides, etc., in these various extracts are described in detail in the original. T. A. H.

**Cholesterol as an Antidote to the Saponins.** ADOLF WINDAUS (*Ber.*, 1909, 42, 238—246).—The action of cholesterol as an antidote to the power of saponins to dissolve blood-corpuscles, discovered by Ransom, has been ascribed to a chemical reaction and to a physical change, such as absorption. The poisons of bees, snakes, and bacterial poisons are similarly counteracted by cholesterol. Digtonin and cholesterol, when mixed in alcoholic solution, immediately give rise to a colourless, crystalline precipitate in fine needles of *digitonin-cholesteride*,  $C_{55}H_{94}O_{23} + C_{27}H_{46}O$ , formed as a simple molecular compound of the two components without any elimination of water. The compound decomposes above  $240^\circ$ ; it is quite impossible to obtain cholesterol from it by prolonged extraction with ether.

It slowly dissociates when boiled in methyl-alcoholic solution for some hours. It is entirely without any solvent action on the blood-corpuscles. Other alcohols behave similarly to cholesterol towards digitonin. Phytosterol forms a molecular compound crystallising in thin needles; the compound with stigmasterol is even less soluble. *Digitonin- $\beta$ -cholestanol* is more soluble than the cholesteride, and crystallises in stellar aggregates of needles.  $\alpha$ -Cholestanol (*cyclocholesterol*) forms no such molecular compound.

*Digitonin-amyl alcohol*, ( $C_{55}H_{94}O_{28} + C_5H_{12}O + 6H_2O$ ) (compare Houdas, Abstr., 1892, 222), is more soluble than the cholesterol derivative. The air-dried product loses amyl alcohol when boiled with water.

*Digitonin-octyl alcohol* behaves similarly. Other alcohols, linalool, geraniol, and sabinol, also combine with digitonin.

Cholesterol esters do not unite with digitonin, nor do these esters counteract the poisonous action of saponins. When digitonin-cholesteride is acetylated, it is easy to remove the cholesterol acetate.

The reaction can be used to detect small quantities of cholesterol and to separate it from mixtures, particularly in cases when cholesterol esters are also present. It is also applicable to the purification of digitonin.

*Solanin-cholesteride* is very sparingly soluble in alcohol, but crystallises with difficulty. *Cyclamin cholesteride* crystallises in minute needles, but the cholesterol can be extracted from this with ether. Cyclamin also gives an insoluble, crystalline additive product with octyl alcohol. From the analysis of this cholesteride, the formula  $C_{36}H_{56}O_{18}$  for cyclamin is obtained. E. F. A.

**Scopoline.** ERNST SCHMIDT (*Arch. Pharm.*, 1909, 247, 79—80).—It was shown previously (Abstr., 1906, i, 104) that scopoline is reduced without difficulty to hydroscopoline, which contains two  $-OH$  groups. Further, on oxidation with chromic acid, scopoline yields pyridine-methochloride, and from these observations the deductions are drawn that the  $-OH$  group of scopoline does not lie in the pyridine nucleus, and that the same applies to the second oxygen atom, which must be present in an ether or morpholine group. In confirmation of this view, it is now shown that hydroscopoline, when carefully oxidised with chromic acid, yields a *methylpiperidinedicarboxylic acid*,



m. p. 214—216° (decomp.), which crystallises in transparent tablets and yields a crystalline, azure-blue *copper salt*. The *hydrochloride*, m. p. 224—225° (decomp.), is crystalline, and the *aurichloride* forms large, yellow leaflets.

$\alpha\alpha'$ -Dimethylpyridine, on oxidation with permanganate, furnishes methylpyridinecarboxylic acid (m. p. 129°) and Ladenburg's  $\alpha\alpha'$ -pyridinedicarboxylic acid. The latter, on electrolytic reduction, furnishes two isomeric hydrogenised acids, of which *one*, m. p. 206—207°, readily passes into the *other*, m. p. 158°, and it is hoped by methylating these acids to synthesise the acid obtained by oxidising hydroscopoline.

T. A. H.

**The Chlorophyll Group. III. New Method of Decomposition in the Chemistry of Chlorophyll.** LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1909, 16, 3—8. Compare Abstr., 1908, i, 439).—The zinc compound obtained by the action of zinc hydroxide and carbon dioxide on an alcoholic solution of chlorophyllan is termed "zinc chlorophyll." It is a complex metallic derivative of chlorophyll, which it closely resembles in properties. Treatment with acids converts the zinc compound into chlorophyllan, whereas alkalis (alcoholic potassium hydroxide) transform it into a substance analogous to alkachlorophyll, the chief difference being that the new compound contains zinc, whereas alkachlorophyll contains magnesium. The name "*zinc-prophyllotaonin*" is suggested. The compound dissolves in ether, yielding a brilliant greenish-blue solution with a red fluorescence. The solution gives five characteristic absorption bands between  $\lambda$  677 and  $\lambda$  492. Treatment of the new compound with concentrated hydrochloric acid yields phyllotaonin or *allophyllotaonin*.  
J. J. S.

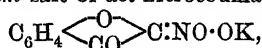
**Rotation of Tannin.** MAXIMILIAN NIERENSTEIN (*Chem. Zeit.*, 1909, 33, 126).—Feist's view (*ibid.*, 1908, 32, 918) that the rotatory power of tannin is due to admixture of dextrose formed by the hydrolysis of a glycolgallic acid is not accepted. Experiments show that specimens of tannin which are free from dextrose have a high rotatory power.  
J. J. S.

**Tannin.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1909, 42, 353—354. Compare Abstr., 1908, i, 40).—Since luteo-acid (pentahydroxydiphenylmethanolidecarboxylic acid) and ellagic acid are produced by the oxidation of tannin, the author has suggested that the production of ellagic acid in plants may be due to oxidation (Abstr., 1908, i, 897). This suggestion is strengthened by the fact that the hot filtered pyridine extract of myrobalan, after dilution with water, boiling, and keeping for thirty hours, yields ellagic acid, whilst the concentrated mother liquor deposits luteo-acid, identical in all respects with that obtained synthetically from tannin.  
C. S.

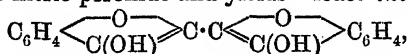
**The So-called "Bloom" of Pyrogallol Tannins and Its Identity with Ellagic Acid.** MAXIMILIAN NIERENSTEIN (*Chem. Zeit.*, 1909, 33, 87. Compare Abstr., 1905, i, 365, 805).—The "bloom" of some samples of sole-leather and of various pyrogallol tannin materials has been examined, and, with but one exception, was conclusively shown to be ellagic acid. The exception is "white mangrove," the bloom of which is laguncurin, a yellow dye.  
W. H. G.

**Coumarandione, the Analogue of Isatin in the Coumarone Series.** RICHARD STOERMER (*Ber.*, 1909, 42, 199—202. Compare Stoermer and Kahlert, Abstr., 1902, i, 457).—It has at last been found possible to prepare coumarandione, the lactone of *o*-hydroxybenzoylformic acid, which is the analogue of isatin in the coumarone series. 1-Nitro-2-diisobutylaminocoumarone, when warmed with alcoholic

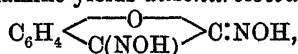
potassium hydroxide, is decomposed with the formation of diisobutylamine and the *potassium* salt of *aci*-nitrocoumaranone,



obtained as lemon-yellow needles. When this salt is treated with an acid, it liberates nitric peroxide and yields "*leuco-oxindigo*,"



obtained as a canary-yellow precipitate, m. p. 276° (decomp.). The *leuco*-compound is oxidised by chromic acid in acetic acid into *coumarandione*,  $\text{C}_8\text{H}_4\text{O}_3$ , which crystallises with  $1\text{H}_2\text{O}$  in small, yellow needles, m. p. 178° (decomp.), and is converted by hot, dilute hydrochloric acid into *o*-hydroxybenzoylformic acid. Coumarandione when acted on by hydroxylamine yields *diisonitrosocoumarone*,



a colourless, crystalline substance, m. p. 203—205°.

W. H. G.

***o*-Hydroxybenzoylformic Acids and Coumarandiones.** KARL FRIES (*Ber.*, 1909, 42, 234—236).—*o*-Hydroxybenzoylformic acid occurs in an anhydrous form and also as monohydrate. The *hydrate* of 2-hydroxy-4-methylbenzoylformic acid crystallises in plates, m. p. 64°; it is faintly yellow, and stable in the atmosphere. The anhydrous acid is more soluble in benzene than the hydrate; it crystallises in feather-like needles, m. p. 102°, which are almost colourless except when viewed in mass. The *hydrate* of 2-hydroxy-5-methylbenzoylformic acid forms yellow prisms, m. p. 75°; the anhydrous acid crystallises in needles, m. p. 107°. These acids lose carbon dioxide and water when heated, forming methylcoumarandiones, but the yield is small and the product difficult to purify. They are conveniently prepared by heating the hydroxybenzoylformic acids in benzene or petroleum solution with an excess of phosphoric oxide for fifteen minutes.

**5-Methylcoumarandione**,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CO}$ , crystallises in well-formed, yellow plates, m. p. 112°. In contact with water it is slowly converted into the hydroxy-acid and goes into solution. It dissolves in concentrated sulphuric acid with a yellowish-red coloration, and on dilution the hydroxy-acid is formed. The ketone reacts immediately with *o*-phenylenediamine, but 2-hydroxy-3-*m*-hydroxy-*p*-tolylquinoxaline, and not methylcoumarophenazine, is formed.

**4-Methylcoumarandione** crystallises in long, golden-yellow prisms, m. p. 149°. These diketocoumarans and the hydroxy-acids give the indophenin reaction with benzene containing thiophen and concentrated sulphuric acid.

E. F. A.

**Method of Preparation of Ketothionaphthens.** KARL AUWERS and F. ARNDT (*Ber.*, 1909, 42, 537—545).—Starting with *p*-tolyl methyl thioether a method is described of obtaining thionaphthen derivatives by using chloroacetyl chloride.

*p*-Tolyl methyl thioether,  $\text{C}_8\text{H}_{10}\text{S}$ , from the sodium salt and methyl

sulphate, is a colourless oil, b. p.  $209^{\circ}/747$  mm.,  $94^{\circ}/31$  mm.,  $D_4^{16}$  1.0302,  $n_D^{16}$  1.57537, which, when heated with chloroacetyl chloride and aluminium chloride in carbon disulphide solution for five hours, and subsequently distilled with steam, is converted into *keto-4-methylthionaphthen*,  $C_6H_4Me \begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix} CH_2$ . It crystallises from petroleum in colourless needles, m. p.  $102^{\circ}$ , which gradually change when moist to carmine-red. On oxidation with potassium ferricyanide in dilute alkali, "4'-*dimethylthioindigotin*,"  $C_{18}H_{12}O_2S_2$ , is formed, which crystallises from nitrobenzene in brownish-red needles, m. p. over  $300^{\circ}$ .

*Ketobenzylidene-methylthionaphthen*,  $C_6H_4Me \begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix} C:CHPh$ , is formed by the condensation of benzaldehyde and ketomethylthionaphthen in alcohol in the presence of hydrogen chloride, and forms long, yellow, glistening needles, m. p.  $145.5^{\circ}$ . The *dibromide*,

$C_{16}H_{12}OBr_2S$ , forms stout, yellow prisms, m. p.  $116^{\circ}$ , and is re-converted into the parent substance by alkali or alcohol.

*Ketobenzylidene-thionaphthen*,  $C_{15}H_{10}OS$ , crystallises from alcohol in yellow needles, m. p.  $131.5^{\circ}$ ; its *dibromide*,  $C_{15}H_{10}OBr_2S$ , forms crystals, m. p.  $114-115^{\circ}$ .

6-*Methylthiol-3-methylacetophenone*,  $SMe \cdot C_6H_4Me \cdot COMe$ , from tolyl methyl thioether, acetyl chloride, and aluminium chloride, crystallises from light petroleum in white needles, m. p.  $51.5^{\circ}$ . It is not hydrolysed by known methods, either being recovered unchanged or suffering decomposition. The 6-thiol-3-methylacetophenone could not be obtained from the thiocresol by a similar method to the methyl ether.

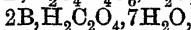
*p-Tolyl chlorothioloacetate*,  $C_6H_4Me \cdot S \cdot CO \cdot CH_2Cl$ , from thiocresol and chloroacetyl chloride, which forms snow-white crystals, m. p.  $38^{\circ}$ , could not be converted into the *o*-chloroacetyl isomeride (compare Fries and Finck, this vol., i, 42). The *acetyl* compound of thiocresol,  $C_9H_{10}OS$ , is an oil, b. p.  $121^{\circ}/14$  mm. W. R.

**Cinchonamine and Certain Other Rare Alkaloids.** BERNARD F. HOWARD and O. CHICK (*J. Soc. Chem. Ind.*, 1909, 28, 53).—The results of trials with cinchonamine hydrochloride as a test for nitric acid and for the estimation of nitrates, by the formation of cinchonamine nitrate, which is nearly insoluble in water, especially in presence of free acid (compare Abstr., 1905. i, 102), are given. Certain data respecting cinchonamine, quinicine, cinchonicine, cupreine, and concusconine are also recorded.

Cinchonamine hydrochloride may be used for the estimation of nitrates in certain cases where other methods present difficulties, and yields results but little inferior to those given by the nitrometer process, but is unsuitable for use in presence of salts of bismuth or other metals which yield insoluble oxychlorides. In aqueous solution 1/100,000 of nitric acid can be detected, and in acetic acid, 1/500.

Cinchonamine,  $C_{19}H_{24}ON_2$ ,  $[\alpha]_D + 120^{\circ}$  in alcohol, does not contain methoxyl. Quinicine,  $C_{20}H_{24}O_2N_2$ ,  $[\alpha]_D + 38^{\circ}40'$  in chloroform, yields a

crystalline *tartrate*,  $B, H_3C_4H_4O_6$ , and *oxalate*,  $2B, H_3C_2O_4, 9H_2O$ , and contains one methoxyl group. Cinchonidine,  $C_{19}H_{22}ON_2, [a]_D + 47^\circ 13'$ , like quinine, could not be obtained crystalline; it does not contain methoxyl. The *tartrate*,  $B, H_3C_4H_4O_6, H_2O$ , and *oxalate*,



are crystalline. Concusconine,  $C_{23}H_{26}O_4N_2, [a]_D + 19^\circ 34'$ , was prepared from cinchonamine residues; it contains two methoxyl groups. Cupreine,  $C_{19}H_{22}O_2N_2, [a]_D - 163^\circ 45'$  in alcohol, contains no methoxyl. The amorphous *platinichloride*,  $B, H_3PtCl_6, H_2O$ , was prepared, but the salt,  $B_3, H_3PtCl_6, 4H_2O$ , referred to by Léger could not be obtained. Cupreine sulphate,  $B_2, H_2SO_4$ , is stated to crystallise with  $6H_2O$ , but this salt prepared under various conditions was found to be anhydrous. The acid sulphate,  $B, H_2SO_4, H_2O$ , crystallises in short, stout, yellow prisms. The disulphate,  $B, 2H_2SO_4, 3H_2O$ , forms short, silky needles and is deliquescent. The hydrochloride,  $B, HCl, H_2O$ , crystallises in small, slightly brown needles, and the dihydrochloride,  $B, 2HCl$ , is also crystalline. The formulæ assigned to these alkaloids were confirmed by determination of the platinum in the respective platinichlorides.

T. A. H.

**Isomerism of Ephedrine and  $\psi$ -Ephedrine.** HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 54—55).—In a previous paper (*Abstr.*, 1908, i, 203) the author has shown that ephedrine is better represented by the formula  $NHMe \cdot CHPh \cdot CHMe \cdot OH$  than by  $OH \cdot CHPh \cdot CHMe \cdot NHMe$ , and that  $\psi$ -ephedrine is an optical isomeride of ephedrine. Gadamer (this vol., i, 49) accepted this, but suggested that the conversion of the one isomeride into the other by the action of hydrochloric acid is probably due to racemisation in the asymmetric complex containing the hydroxyl group, rather than in that containing the methylimino-grouping. The author now points out that this explanation is not excluded by his former paper, and that he left this point as an open question.

T. A. H.

**Crystallography of the Ephedrine, Damascenine, and Aconitine Groups.** K. SCHWANTKE (*Zeitsch. Kryst. Min.*, 1909, 46, 73—115).— $\psi$ -Ephedrine, rhombic [ $a:b:c = 0.84492:1:1.8598$ ]. Ephedrine hydriodide, rhombic [ $a:b:c = 0.73703:1:0.28643$ ].  $\psi$ -Ephedrine hydriodide, rhombic [ $a:b:c = 0.60282:1:1.3722$ ]. Methylephedrine methiodide, rhombic [ $a:b:c = 0.97926:1:0.76088$ ]. Methyl- $\psi$ -ephedrine methiodide, rhombic [ $0.64227:1:1.2088$ ].

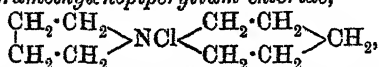
Damascenine hydrochloride, triclinic [ $a:b:c = 0.66527:1:0.45318$ ;  $\alpha = 89^\circ 51'$ ;  $\beta = 103^\circ 30'$ ;  $\gamma = 89^\circ 11'$ ]; hydrobromide, monoclinic [ $a:b:c = 2.7575:1:2.4825$ ;  $\beta = 100^\circ 6'$ ]; hydriodide, monoclinic [ $a:b:c = 2.7519:1:2.4372$ ;  $\beta = 99^\circ 27'$ ].

Aconitine, rhombic [ $a:b:c = 0.54492:1:0.38917$ ]; hydrobromide, rhombic [ $a:b:c = 0.86455:1:1.3095$ ]; hydrochloride, rhombic [ $a:b:c = 0.87488:1:1.3040$ ]. Picroaconitine could not be obtained crystalline. Methylpicroaconitine, rhombic [ $a:b:c = 0.99572:1:1.31416$ ]. Ethylpicroaconitine, rhombic [ $a:b:c = 0.07952:1:1.2700$ ]. Aconine hydrochloride, monoclinic [ $a:b:c = 0.63461:1:1.0374$ ;  $\beta = 90^\circ$ ].

L. J. S.

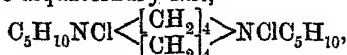
**Dicyclic Quaternary Bases.** AUGUST ALBERT (*Ber.*, 1909, 42, 545—556).—It has been shown by Gabriel and Colman (*Abstr.*, 1906, i, 881) that when evaporated with water  $\gamma$ -chloropropylpiperidine is transformed into the quaternary salt, and that the reaction is a reversible one. This paper deals with the preparation of a dicyclic quaternary salt containing one more methylene group in one of the rings. 1- $\delta$ -Phenoxybutylpiperidine,  $\text{OPh} \cdot [\text{CH}_2]_4 \cdot \text{C}_5\text{NH}_{10}$ , obtained by heating  $\delta$ -chlorophenoxybutane with piperidine for four hours at  $100^\circ$ , distils at  $316\text{--}320^\circ$ . It is purified by means of the *hydriodide*,  $\text{C}_{15}\text{H}_{23}\text{ON} \cdot \text{HI}$ , which forms white, feathery needles, m. p.  $147^\circ$ ; the *hydrochloride* has m. p.  $156^\circ$ , the *hydrobromide*, m. p.  $159^\circ$ , the *picrate*, m. p.  $120\text{--}121^\circ$ , the *mercurichloride*, m. p.  $138^\circ$ , and the *gold salt*, m. p.  $121^\circ$ . When the hydrochloride is heated with hydrochloric acid in a sealed tube at  $150^\circ$  for five hours, 1- $\delta$ -chlorobutylpiperidine hydrochloride,  $\text{CH}_2\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{C}_5\text{NH}_{10} \cdot \text{HCl}$ , is formed quantitatively; it crystallises in white plates from acetone, m. p.  $162^\circ$ ; the *aurichloride*,  $\text{C}_9\text{H}_{19}\text{NCl}_5\text{Au}$ , has m. p.  $93^\circ$ , the *picrate*, m. p.  $132^\circ$ .  $\delta$ -Bromobutylpiperidine hydrobromide,  $\text{C}_9\text{H}_{19}\text{NBr}_2$ , prepared in a similar manner, forms plates, m. p.  $162.5^\circ$ .

A cold ethereal solution of  $\delta$ -chlorobutylpiperidine is quickly converted into *tetramethylenepiperylum chloride*,

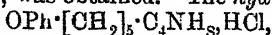


which forms white, hygroscopic leaflets; the *aurichloride*,  $\text{C}_9\text{H}_{18}\text{NCl}_4\text{Au}$ , has m. p.  $245^\circ$ , the *picrate*,  $\text{C}_{15}\text{H}_{20}\text{O}_7\text{N}_4$ , m. p.  $232^\circ$ , the *mercurichloride*,  $\text{C}_9\text{H}_8\text{NCl}_6\text{HgCl}_2$ , m. p.  $229^\circ$ , the *platinichloride*, m. p.  $237^\circ$ . Alkali converts  $\delta$ -bromobutylpiperidine hydrobromide at once into the quaternary salt.

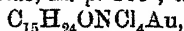
That it is not the diquaternary salt,



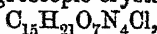
is proved by its synthesis from  $\epsilon$ -chloropentylpyrrolidine, whereas if diquaternary salts were obtained in such reactions, the isomeric compound,  $\text{C}_4\text{H}_9\text{NCl} \left\langle \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \right\rangle_5 \text{NClC}_4\text{H}_9$ , would be the result. This was accomplished by heating  $\epsilon$ -chlorophenoxy-pentane with pyrrolidine at  $100^\circ$  for four hours, when  $\epsilon$ -phenoxy-pentylpyrrolidine, which distils at  $317\text{--}318^\circ/760\text{ mm.}$ , was obtained. The *hydrochloride*,



has m. p.  $139^\circ$ , the *hydriodide*, m. p.  $109^\circ$ , the *aurichloride*,



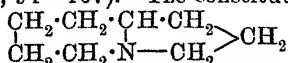
m. p.  $109^\circ$ , and the *picrate*, m. p.  $99\text{--}100^\circ$ .  $\epsilon$ -Chloropentylpyrrolidine forms light yellow, very hygroscopic crystals; the *picrate*,



and *picrolonate* have been prepared. The base undergoes in ethereal solution isomeric change into the tetramethylpiperylum chloride. This quaternary salt does not give  $\delta$ -chlorobutylpiperidine on evaporation of its aqueous solution, thus proving more stable than the trimethylene compound.

W. R

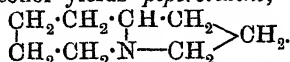
**Synthesis of Inactive  $\delta$ -Coniceine.** KARL LÖFFLER and HANS KAIM (*Ber.*, 1909, 42, 94—107).—The constitution



suggested by Lellmann (*Abstr.*, 1890, 1328) for  $\delta$ -coniceine has been confirmed by direct synthesis.

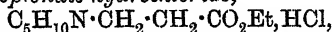
Pyridylacrylic acid (Einhorn, *Abstr.*, 1892, 77), when reduced by Ladenburg's method with sodium and alcohol, yields piperidylpropionic acid, which was isolated in the form of the hydrochloride of the ethyl ester.

The free acid when distilled under reduced pressure yields the lactim, 2-piperolidone,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \qquad \qquad \qquad \diagup \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} - \text{CO} \end{array}$ , which on reduction with sodium and alcohol yields piperolidine,



This is identical with inactive  $\delta$ -coniceine, which was prepared from *i*-coniine by a process similar to that used by Lellmann in the preparation of active  $\delta$ -coniceine.

*Ethyl piperidylpropionate hydrochloride*,



crystallises from acetone in glistening, colourless needles, m. p. 122°. The *aurichloride*,  $\text{C}_{10}\text{H}_{19}\text{O}_2\text{N} \cdot \text{HAuCl}_4$ , forms yellow needles, m. p. 127—128°; the *platinichloride* has m. p. 127—130°. The free ester has b. p. 143—144°/21 mm. and  $D_4^{15}$  1.0214, and is hydrolysed by hot hydrochloric acid to the *hydrochloride* of the acid,  $\text{C}_8\text{H}_{15}\text{O}_2\text{N} \cdot \text{HCl}$ , which melts at 188°. The *aurichloride*,  $\text{C}_8\text{H}_{15}\text{O}_2\text{N} \cdot \text{HAuCl}_4$ , has m. p. 151°, and the *platinichloride*, 197°. The acid crystallises from water in large, rectangular plates containing water of crystallisation. It begins to sinter at 70°, and melts at 105°, or, when anhydrous, at 147—148°.

2-Piperolidone has b. p. 126—127°/12 mm., or 263—264°/760 mm., and  $D_4^{15}$  1.0715. The *hydrochloride* is hygroscopic; the *platinichloride*,  $(\text{C}_8\text{H}_{15}\text{ON})_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ , forms large, hexagonal plates, and has m. p. 138°; the *aurichloride* is oily.

Piperolidine has b. p. 161° and  $D_4^{15}$  0.904, and its aqueous solution is strongly alkaline. The *picrate*,  $\text{C}_8\text{H}_{15}\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , has m. p. 226°; the *hydrochloride* is hygroscopic; the *aurichloride* crystallises in compact needles, m. p. 192°, after sintering at 189°; the *platinichloride* melts and decomposes at 213°; the *mercuric* salt has m. p. 235—238°. The *ethiodide* is formed immediately on the addition of ethyl iodide to an ethereal solution of the base, and the corresponding *platinichloride*,  $(\text{C}_8\text{H}_{15}\text{NEt})_2 \cdot \text{PtCl}_6$ , begins to decompose at 218°, and has m. p. 229—230°.

3-Hydroxy-2-piperolidone,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \qquad \qquad \qquad \diagup \text{CH} \cdot \text{OH} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} - \text{CO} \end{array}$ , is obtained

when Einhorn's  $\alpha$ -pyridyllactic acid is reduced and the aqueous solution of the resulting acid evaporated. It separates from acetone in colourless crystals, m. p. 129—130°, b. p. 183—184°/18 mm. or

304—305°/760 mm. The *aurichloride*,  $C_8H_{13}O_2N, HAuCl_4$ , m. p. 89—90°, and the *platinichloride*,  $(C_8H_{13}O_2N)_2, H_2PtCl_6$ , m. p. 92—94°, are both readily soluble in water. J. J. S.

**Synthesis of  $\beta$ -Coniceine (*l*- $\alpha$ -Allylpiperidine).** KARL LÖFFLER and GOTTHOLD FRIEDRICH (*Ber.*, 1909, 42, 107—116).—2- $\beta$ -Hydroxypropylpiperidine (Ladenburg, *Abstr.*, 1890, 68), when heated at 100° with phosphoric oxide, yields a mixture of two isomeric secondary bases, one of these is a solid, m. p. 18°. This can be resolved into active components, the *l*-form of which is identical with  $\beta$ -coniceine (Löffler, *Abstr.*, 1905, i, 917), which is thus shown to be *l*- $\alpha$ -allylpiperidine. The isomeric base, *iso*- $\alpha$ -allylpiperidine, which can be isolated from the alcoholic mother liquors of the picrate of the solid base, can also be resolved into active components by means of the hydrogen tartrates.

2- $\beta$ -Hydroxypropylpiperidine forms a *picrate*, m. p. 111—112°, a *platinichloride*, m. p. 148—149°, and an *aurichloride*, m. p. 136—137°.

*$\alpha$ -Allylpiperidine* forms a well-defined *picrate*,  $C_8H_{15}N, C_6H_5O_7N_3$ , m. p. 113—114.5°. The *hydrochloride*,  $C_8H_{15}N, HCl$ , crystallises in glistening plates, sparingly soluble in acetone, m. p. 206—207°. The *aurichloride* has m. p. 107—108°, and the *platinichloride*, m. p. 184°. The free base has m. p. 18°, b. p. 168.5—170°/753 mm., and  $D_4^{15}$  0.8716. It readily reduces permanganate, and yields a nitroso-amine with nitrous acid. It combines with hydrogen iodide, and the additive compound when reduced yields  $\alpha$ -propylpiperidine. The *d*-tartrate of the *d*-base is less soluble than that of the *l*-base; it has m. p. 39° and  $[\alpha]_D^{25} + 49.89$ .

*iso*- $\alpha$ -Allylpiperidine yields an oily *picrate*. The *hydrochloride*,  $C_8H_{15}N, HCl$ , has m. p. 186—187°, and is stable when exposed to the air; the *platinichloride* has m. p. 138—139°, and the base has b. p. 166.5—168.5° and  $D_4^{15}$  0.8695. The *d*-hydrogen tartrate,

$C_8H_{15}N, C_4H_6O_6$ , has m. p. 70—71°. The base from the tartrate has  $[\alpha]_D + 24.81^\circ$  at 15°, and the corresponding *hydrochloride*, m. p. 189—190°. The liquid base, obtained together with  $\beta$ -coniceine by the elimination of water from conhydrine, has  $[\alpha]_D - 25.5^\circ$ , and its hydrochloride has m. p. 189—190°. This base can be partly transformed into  $\beta$ -coniceine by saturating with hydrogen chloride at -16°, heating in sealed tubes at 100° for several hours, and then eliminating hydrogen chloride. When reduced by Ladenburg's method, solid  $\beta$ -coniceine yields *l*-coniine, and this affords a simple method of passing from conhydrine to *l*-coniine. J. J. S.

**Constitution of  $\psi$ -Conhydrine.** KARL LÖFFLER (*Ber.*, 1909, 42, 116—124. Compare Ladenburg and Adam, *Abstr.*, 1891, 1119).— $\psi$ -Conhydrine and conhydrine are readily separated by means of their hydrochlorides; the salt derived from conhydrine is extremely hygroscopic; whereas that from the  $\psi$ -base crystallises well from alcohol and has m. p. 212—213°. The  $\psi$ -base has m. p. 105—106° (not 100—102°), b. p. 236—236.5°, and  $\alpha_D + 10.98^\circ$  to  $+ 11.06^\circ$ . It crystallises from anhy-

drous ether in extremely slender needles, but from moist ether in hydrated plates, m. p. about  $80^{\circ}$ . Engler and Bauer's statement (Abstr., 1894, i, 471), that  $\psi$ -conhydrine can be transformed into conhydrine by simply preparing the gold salt and decomposing this in the usual manner, is not confirmed.

$\psi$ -Conhydrine aurichloride,  $C_8H_{17}ON, AuCl_4$ , has m. p.  $133-134^{\circ}$ , and the platinichloride forms slender, golden-yellow needles, m. p.  $185-186^{\circ}$ .

$\psi$ -Conhydrine is an hydroxyconiine, since when treated with hydriodic acid a  $\psi$ -iodoconiine is obtained, which on reduction yields *d*-coniine, whereas conhydrine under similar conditions yields *l*-coniine. Conhydrine and  $\psi$ -conhydrine are not stereoisomeric, as the latter yields no trace of  $\beta$ -coniceine or its oily isomeride (compare preceding abstract). Similarly, when the  $\psi$ -base is transformed into the iodo-derivative and hydrogen iodide is eliminated from this, no trace of the dicyclic  $\delta$ -coniceine is formed. It is shown that the hydroxyl group of the  $\psi$ -base cannot be present in the side-chain, and must thus be attached to a carbon atom of the nucleus, probably in the  $\gamma$ -position.

The  $\psi$ -coniceine,  $C_8H_{15}N$ , obtained by the action of phosphoric oxide on  $\psi$ -conhydrine at  $100-120^{\circ}$ , has b. p.  $171-172^{\circ}$ ,  $D_4^{15} 0.8776$ , and  $[\alpha]_D + 122.6^{\circ}$  at  $15^{\circ}$ . It does not dissolve readily in water, decolorises permanganate, and forms a nitrosamine. Its hydrochloride crystallises from a mixture of alcohol and acetone, and has m. p.  $205-206^{\circ}$ . The platinichloride has m. p.  $153-154^{\circ}$ , and the aurichloride is an oil. The iodoconhydrine, obtained by the action of hydriodic acid on  $\psi$ -conhydrine, yields a hydriodide,  $C_8H_{16}NI, HI$ , m. p.  $216-217^{\circ}$ , whereas the isomeric compound, obtained by the addition of hydrogen iodide to  $\psi$ -coniceine, has m. p.  $182^{\circ}$ . J. J. S.

$\psi$ -Conhydrine. CARL ENGLER (Ber., 1909, 42, 559. Compare Engler and Bauer, Abstr., 1894, i, 471).—As Löffler (preceding abstract) has shown that Ladenburg and Adam's  $\psi$ -conhydrine (Abstr., 1891, i, 1119) is a solid solution of conhydrine and  $\psi$ -conhydrine, there is no foundation for the supposed conversion of the pseudo-compound into conhydrine.

W. R.

4-Picolylalkine [4- $\beta$ -Hydroxyethylpyridine], 4-Pipecolylalkine [4- $\beta$ -Hydroxyethylpiperidine, and Quinuclidine. KARL LÖFFLER and FRITZ STIEFEL (Ber., 1909, 42, 124-132).—4-Methylpyridine condenses readily with 40% formaldehyde solution, yielding Koenigs and Happe's trimethylol derivative (Abstr., 1903, i, 851), but with a 20% aldehyde solution at  $135-140^{\circ}$  it yields the monomethylol derivative, 4- $\beta$ -hydroxyethylpyridine,  $C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot OH$ , as a colourless syrup,  $D_4^{15} 1.1016$  and b. p.  $125-126^{\circ}/15$  mm. It is most readily purified by means of the picrate,  $C_{13}H_{12}O_8N_4$ , which forms compact, dark yellow crystals, m. p.  $122-123^{\circ}$ . The platinichloride forms crystalline plates, m. p.  $164^{\circ}$  (decomp.), readily soluble in water. The aurichloride has m. p.  $124-125^{\circ}$ . When heated with hydriodic acid and red phosphorus, 4- $\beta$ -hydroxyethylpyridine yields the oily iodide,  $C_5NH_4 \cdot CH_2 \cdot CH_2 \cdot I$ . The corresponding picrate forms long, refractive prisms, m. p.  $108-110^{\circ}$ , and the platinichloride forms pale yellow needles, m. p.  $147-148^{\circ}$ . When warmed, the iodide is readily

transformed into the isomeric *pyridonium iodide*,  $\text{C} \begin{array}{c} \text{CH-CH} \\ \text{CH}_2\text{-CH}_2 \\ \text{CH=CH} \end{array} \text{NI}$

(compare Abstr., 1905, i, 265), which crystallises from dilute alcohol in minute, colourless needles, m. p. 216—218°. The corresponding *chloride* forms minute crystals, and the *platinichloride*,  $(\text{C}_7\text{H}_8\text{N})_2\text{PtCl}_6$ , an insoluble, flesh-coloured precipitate, decomposing at about 300°. It has not been found possible to transform Happe's tri-iodohydrin from the trimethylol derivative into an isomeric pyridonium salt.

4- $\beta$ -*Hydroxyethylpiperidine*,  $\text{NH} \begin{array}{c} \text{CH}_2\text{-CH}_2 \\ \text{CH}_2\text{-CH}_2 \end{array} \text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , obtained by reducing the corresponding pyridine derivative by Ladenburg's method, has b. p. 120—125°/15 mm. or 227—228°/760 mm. and  $D_4^{20}$  1.0059. It has an intense odour of semen. The *aurichloride*,  $\text{C}_7\text{H}_{15}\text{ON}\cdot\text{HAuCl}_4$ , forms large, compact crystals, m. p. 108—110°; the *picrate* is oily. With hydriodic acid and phosphorus the base yields the *hydriodide*,  $\text{C}_7\text{H}_{13}\text{NI}\cdot\text{HI}$ , which crystallises from hot water in needles, m. p. 158—159°. The iodo-base is readily transformed

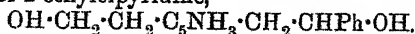
into the *quinuclidine hydriodide*,  $\text{CH} \begin{array}{c} \text{CH}_2\text{-CH}_2 \\ \text{CH}_2\text{-CH}_2 \\ \text{CH}_2\text{-CH}_2 \end{array} \text{NHI}$ , when its

ethereal solution is boiled. The hydriodide forms a colourless syrup readily soluble in water. The *picrate* crystallises in slender, pale yellow needles. The *base*,  $\text{C}_7\text{H}_{13}\text{N}$ , has b. p. 140—141° and  $D_4^{20}$  0.9139. It does not decolorise permanganate, and forms an *ethiodide*, which is hygroscopic. The *platinichloride*,  $(\text{C}_7\text{H}_{13}\text{N})_2\text{PtCl}_6$ , has m. p. 212°.

J. J. S.

Condensation of 2:6-Lutidine with Formaldehyde and Derivatives of 2-Methyl-6-methylolpyridine. KARL LÖFFLER and FRITZ THIEL (*Ber.*, 1909, 42, 132—140. Compare Koenigs and Happe, Abstr., 1903, i, 850). 2-Methyl-6-ethylolpyridine distils at 121—122°/12 mm., and has m. p. about 55°. It does not decolorise permanganate, and yields a *picrate* which crystallises in pale yellow needles, m. p. 102—102.5°. The *platinichloride* has m. p. 183—185° (decomp.).

In the preparation of the monohydroxy-derivative an appreciable amount of a *dihydroxy*-compound,  $\text{C}_8\text{H}_{13}\text{O}_2\text{N}$ , is formed. This crystallises from a mixture of chloroform and ether in colourless prisms, m. p. 73—74.5° and b. p. 185.5—186°/15 mm. The *picrate* crystallises from alcohol in yellow needles, m. p. 133.5—134.5°. The *platinichloride*,  $(\text{C}_8\text{H}_{13}\text{O}_2\text{N})_2\cdot\text{H}_2\text{PtCl}_6$ , has m. p. 171—173° (decomp.), and the *aurichloride*, m. p. 141—142°. When oxidised with nitric acid the base yields dipicolinic acid, and hence is presumably 2:6-*diethylolpyridine*. 2-Methyl-6-ethylolpyridine condenses with benzaldehyde at 125—130° yielding a brown oil, the *platinichloride* of which decomposes at 200—206°. This condensation product is probably 6-phenylmethylol-2-ethylolpyridine,



When heated at 125—130° with hydrobromic acid which has been saturated at 0°, the methylethylol derivative yields 2-methyl-6-bromo-

*ethylpyridine*. The *picrate*,  $C_8H_{10}NBr, C_6H_3O_3N_3$ , crystallises from benzene in slender prisms, m. p. 111°; the *platinichloride* separates from water in compact, pointed crystals, m. p. 183—184° (decomp.), and the *aurichloride* forms reddish-yellow needles, m. p. 159—162° (decomp.). The free base is slowly isomerised to the *pyridonium*

*bromide*,  $\begin{array}{c} CH:CH-C-CH_2 \\ | \\ CH:CMc-NBr-CH_2 \end{array}$ , which crystallises from acetone in snow-white needles, m. p. 155—156°.

2-Methyl-6-ethylpyridine is obtained when the methyl-bromoethylpyridine is reduced with zinc dust and hydrochloric acid; it is usually accompanied by a certain amount of methylvinylpyridine, which can be removed by treatment with acidified *N*/100 permanganate. The pure methylethyl derivative is a colourless liquid, b. p. 160—161·5°/760 mm. and  $D^{15}_D 0.9229$ . The *picrate*,  $C_8H_{11}N, C_6H_3O_7N_3$ , forms yellow plates, m. p. 127—127·5°; the *platinichloride*, small crystals, m. p. 188—190° (decomp.), and the *aurichloride*, yellow needles, m. p. 127·5—128·5°.

When reduced by Ladenburg's method, the base yields two stereoisomeric 2-methyl-6-ethylpiperidines, which can be separated by means of their *hydrochlorides*,  $C_8H_{17}N, HCl$ . Of these, one is sparingly soluble in acetone, and forms long, snow-white needles, m. p. 153·5—154°.

The corresponding *platinichloride*,  $(C_8H_{17}N)_2, H_2PtCl_6$ , forms well developed prisms, m. p. 188—190°, and is readily soluble in water. The *aurichloride* has m. p. 134°, and the *picrate* forms long needles, m. p. 135°. The free base has b. p. 151—151·5°/755 mm. (corr.) and  $D^{14.5}_D 0.8306$ . The base can be resolved into its active components by crystallising the acid tartrates. The sparingly soluble *tartrate*, m. p. 58—59°, gives a base with  $[\alpha]^{25}_D +13.97^\circ$ . The *platinichloride* of the active base decomposes at 204—206°; the *aurichloride* has m. p. 133·5—134·5°, and the *hydrochloride*, m. p. 287—288°.

The *hydrochloride*, which is readily soluble in acetone, forms needles, m. p. 171·5—172·5°. The *platinichloride* has m. p. 196—197°, and the base, iso-2-methyl-6-ethylpiperidine, is a colourless liquid, b. p. 157—158°/760 mm. and  $D 0.845$ . The *picrate* has m. p. 101·5—102°, and the *aurichloride* is an oil. The base can be resolved by means of camphorsulphonic acid, but the acid tartrates are syrups. J. J. S.

*N*-Hydroxydioxindole: Trioxindole. GUSTAV HELLER [with JULIUS SÖLLING] (*Ber.*, 1909, 42, 470—479).—Reissert has already prepared *N*-hydroxyindole (*Abstr.*, 1896, i, 389; this vol., i, 51). *N*-Hydroxydioxindole (*trioxindole*),  $C_8H_4 \begin{array}{c} CH(ON) \\ \diagup \quad \diagdown \\ N(OH) \end{array} CO$ , is obtained when ammonium *o*-nitromandelate is reduced with zinc dust and water in the presence of ammonium chloride and then acidified with hydrochloric acid. It crystallises from water in colourless prisms, sinters at 167°, and melts and decomposes at 172°. The aqueous solution has an acid reaction, gives a blue coloration with ferric chloride, and reduces Fehling's solution in the cold. Alkalis decompose the compound, and in the presence of atmospheric oxygen, anthroxanic acid is formed; if an excess of alkali is present, isatin is also formed.

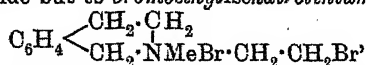
Trioxindole is converted into *N*-hydroxyisatin when its acetone solution is oxidised with a dilute acetic acid solution of permanganate; acetoxindole under similar conditions yields isatin. Oxidation with a hot alkaline solution of permanganate converts trioxindole into azoxybenzoic acid, and reduction with zinc dust and acetic acid yields isatyd (Heller, Abstr., 1904, i, 516).

*Acetoxindole*,  $C_{10}H_9O_4N$ , crystallises from benzene in prisms, which turn red at  $100^\circ$  and then melt at  $125^\circ$ . Its alkaline solutions deposit salts of isatoic acid when kept, and its aqueous solution yields isatin when boiled. The *N*-benzoyl derivative,  $C_8H_6O_3N \cdot C_6H_5$ , obtained by the action of benzoyl chloride in the presence of aqueous sodium acetate solution, has m. p.  $126^\circ$ . A different benzoyl derivative is obtained by benzoylating in pyridine solution; it has m. p.  $152^\circ$ .

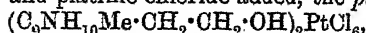
With hydrazine sulphate and sodium acetate solution the trioxindole yields a compound,  $C_8H_9O_2N_2$ , m. p.  $243^\circ$ , which is insoluble in alkalis; the mother liquors from the compound yield isatinhydrazine. With phenylhydrazine a compound,  $C_{20}H_{17}N_5$ , is obtained. It crystallises from alcohol in large, pliable plates, m. p.  $226^\circ$ . *Isatinosazone*, which is isomeric with this compound, crystallises from a mixture of chloroform and light petroleum in slender, reddish-brown needles, m. p.  $183^\circ$  (decomp.).

J. J. S.

**Asymmetric Nitrogen. XXXV. One-sided Addition of a Tertiary Base to a Dihalogenide.** EDGAR WEDKIND (*Ber.*, 1909, 42, 300—303).—The author attempted to synthesise an optically active compound containing two asymmetric nitrogen atoms. A completely analogous compound to tartaric acid is scarcely possible, but it was hoped to prepare one in which the nitrogen atoms were separated by one or more methylene groups. It was found, however, that interaction of ethylene bromide with *isokairolin* (*N*-methyltetrahydroisoquinoline) does not lead to the formation of ethylenebis-*isokairolinium* bromide but to *bromoethylisokairolinium bromide*,



which crystallises from a mixture of alcohol and ether, decomp.  $183^\circ$ . This compound has no further action on *isokairolin*, and this inability to form a further additive compound is ascribed to steric hindrance. The *iodide*,  $C_{12}H_{17}NBrI$ , readily obtained from potassium iodide and an aqueous solution of the bromide, crystallises from ether, and if the iodide or bromide is shaken with moist silver oxide, neutralised with hydrogen chloride, and platinic chloride added, the *platinichloride*,

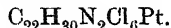


is precipitated. *N*-Ethyltetrahydroisoquinoline has no action on ethylene bromide, and ethylene iodide gives with *isokairolin* an abnormal salt.

*Ethylenebis-isokairolinium iodide*,

$$C_6H_4 \begin{cases} CH_2 - CH_2 \\ | \\ CH_2 \cdot NMeBr \cdot CH_2 \cdot CH_2 \cdot NMeBr \end{cases} \begin{cases} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot C_6H_4 \end{cases}$$
 easily obtained from ethylenebistetrahydroisoquinoline (1 mol.) and

methyl iodide (2 mols.), separates from alcohol as a crystalline powder, decomp.  $232^{\circ}$ , and the free base forms the *platinichloride*,



The dicamphorsulphonate, from the iodide and silver *d*-camphorsulphonate in moist acetone, could not be resolved into fractions of differing rotatory power, and the regenerated iodide is inactive. W. R.

**5-Methylisooxazole.** LUDWIG CLAISEN (*Ber.*, 1909, 42, 59—68).—The substance b. p.  $103\text{--}105^{\circ}/20$  mm., obtained by Schmidt and Widmann (*Abstr.*, 1908, i, 456), and designated 5-methylisooxazole, cannot be such. The author has already prepared 5-methylisooxazole, b. p.  $122^{\circ}$  or  $29\text{--}30^{\circ}/20$  mm. (*Abstr.*, 1892, 1072). In the isooxazoles, as in other homologous series, the b. p. of the methyl derivative must lie between those of the parent substance and of the dimethyl derivative. *isooxazole* has b. p.  $95.5^{\circ}$ , and dimethylisooxazole,  $141\text{--}142^{\circ}$ . A substance of b. p.  $103\text{--}105^{\circ}/20$  mm. would have b. p. above  $200^{\circ}$  under atmospheric pressure, and consequently cannot be a methylisooxazole. Moreover, Schmidt and Widmann's substance does not possess the unpleasant odour of pyridine which is so characteristic of the lower isooxazoles.

The author contributes the following new properties in connexion with the methylisooxazoles. The sesquioxime,  $\text{C}_8\text{H}_{13}\text{O}_3\text{N}_3$ , obtained previously (*Abstr.*, 1891, 416), is decomposed by warm *N*/2-hydrochloric acid, yielding pure 5-methylisooxazole, whilst with concentrated hydrochloric acid a mixture is obtained of 80% of 3-methylisooxazole and 20% of 5-methylisooxazole, from which the latter is easily removed by treatment with sodium ethoxide (*Abstr.*, 1904, i, 14).

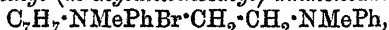
5-Methylisooxazole, in aqueous-alcoholic solution, forms with platinic chloride a yellow, crystalline compound,  $(\text{C}_4\text{H}_5\text{ON})_2\text{PtCl}_4$ , m. p.  $210\text{--}212^{\circ}$ , and a white, crystalline *mercurichloride*,  $\text{C}_4\text{H}_5\text{ON} \cdot \text{HgCl}_2$ , and *cadmichloride*,  $\text{C}_4\text{H}_5\text{ON} \cdot \text{CdCl}_2$ , with aqueous mercuric and cadmium chlorides respectively. In dilute aqueous potassium hydroxide, 5-methylisooxazole forms a clear solution of potassium cyanoacetone, from which phenylhydrazine hydrochloride precipitates cyanoacetone-phenylhydrazone. Sodium cyanoacetone is obtained quantitatively as a white, crystalline precipitate by adding alcoholic sodium ethoxide to a dilute ethereal solution of 5-methylisooxazole, and in aqueous-alcoholic solution yields with diazobenzene chloride a yellow, crystalline phenylazocyanoacetone, and with aniline hydrochloride, cyanoacetoneanilide. 5-Methylisooxazole yields  $\beta$ -iminobutyronitrile by heating at  $100^{\circ}$  with alcoholic ammonia; 5-amino-1-phenyl-3-methylpyrazole by prolonged heating with phenylhydrazine, and with methyl iodide at  $100^{\circ}$  a *methiodide*,  $\text{C}_4\text{H}_5\text{ONMeI}$ , m. p.  $125\text{--}126^{\circ}$ , which in cold aqueous solution is converted by silver oxide into acetoacetyl-methylamide, the *N*-benzoyl derivative of which,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NMeBz}$ , m. p.  $107^{\circ}$ , is obtained by slowly warming 5-methylisooxazole and methyl sulphate at  $70^{\circ}$ , pouring the product into water, and adding a solution of potassium benzoate.

The preceding reactions are quoted by the author as additional evidence for the correctness of the constitution of his 5-methylisooxazole. C. S.

Asymmetric Nitrogen. XXXVI. Quaternary Amino-ammonium Salts, a New Type of Asymmetric Nitrogen. EDGAR WEDEKIND and WOLDEMAR MEYER (*Ber.*, 1909, 42, 303—309).

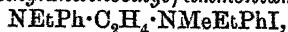
—The result of the experiments on *isokairoline* (this vol., i, 184) lead to the examination of other ditertiary bases with regard to their additional activity towards alkyl haloids. The type employed was  $\text{Ph} \begin{smallmatrix} \diagup \\ \alpha \end{smallmatrix} \text{N} \cdot [\text{CH}_2]_x \cdot \text{N} \begin{smallmatrix} \diagdown \\ \alpha \end{smallmatrix} \text{Ph}$ ; when  $x=2$  and  $\alpha$  is Et, benzyl bromide gives no additive compound; when  $x=3$  and  $\alpha$  is Me, then benzyl bromide is quickly taken up by both tertiary nitrogen atoms; if  $x=2$  and  $\alpha$  is Me, then only one molecule of benzyl bromide is absorbed to form a monoquaternary salt. An analogous amino-ammonium salt is formed from diphenyldimethylethylenediamine and methyl iodide; the diquaternary salt can be obtained indirectly, however, by the action of methyl sulphate and subsequent conversion of the methyl sulphate salt into di-iodide. The diquaternary or the amino-ammonium salt can be obtained from allyl iodide and diphenyldimethylpropylenediamine according to the conditions. The conclusion is drawn that the inability to form diquaternary salts in the case of dimethylene compounds is due to steric hindrance (*loc. cit.*), and that the lengthening of the chain to three methylene groups enables the latent additive activity of the other nitrogen atom to become operative. The high molecular rotatory power of the amino-ammonium salts examined is in accordance with their high degree of asymmetry.

*Phenylbenzylmethyl-(methylanilinoethyl)-ammonium bromide,*



from diphenyldimethylethylenediamine and benzyl bromide, is obtained in 59% yield, and is crystallised from acetone containing a little alcohol, decomp. 119—139°. Once with excess of bromide a *dibromide*,  $\text{C}_{30}\text{H}_{34}\text{N}_2\text{Br}_2$ , was formed, decomp. 124—125°. The amino-ammonium compound is very easily resolved into its optical antipodes, as the solubility of the *l*-base-*d*-camphorsulphonate in methyl alcohol is very much less than the *d*-compound. The extreme  $[\text{M}]_D$  of the fractions for the ions were  $-442^\circ$  and  $+417^\circ$ . The two camphorsulphonates form snow-white needles, decomp. 125°. The *d*-base-*d*-bromocamphorsulphonate is the less soluble salt when the bromo-compound is used. The *l*-amino-ammonium *iodide*,  $\text{C}_{23}\text{H}_{27}\text{N}_2\text{I}$ , forms rhombic plates, decomp. 115°,  $[\text{M}]_D -411.5^\circ$  in alcohol and  $[\text{M}]_D -424.6^\circ$  in chloroform. The *d*-*iodide* has  $[\text{M}]_D +403.2^\circ$  in alcohol, and undergoes autoracemisation in solution; the velocity constant in 50% alcohol-chloroform solution is  $K=0.00024$ , and in 96% alcohol,  $K=0.000033$ . The rate is, therefore, much slower in alcohol than in chloroform, but that it takes place in alcohol which has a high dielectric constant is surprising in the light of Wedekind and Paschke's work (*Abstr.*, 1908, i, 722). As benzyl bromide can be detected in the inactive solution, the conclusion drawn previously, that racemisation is due to decomposition and not to intramolecular change, is supported.

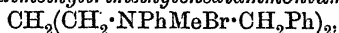
*Phenylmethylethyl-(ethylanilinoethyl)-ammonium iodide,*



obtained from diphenyldiethylethylenediamine and methyl iodide in a closed tube heated at 80° for six hours, crystallises from ether, decomp.

180°, and the symmetrical compound,  $C_2H_4(NPhMeEtI)_2$ , from diphenyl-diethylethylenediamine and methyl sulphate at 120° and precipitation by potassium iodide, is yellow, decomp. 119—120°.

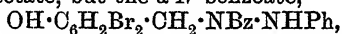
*Diphenyldibenzyltrimethylaminium dibromide*,



forms colourless crystals, decomp. 195—197°. The dicamphor-sulphonate is well characterised.

W. R.

**Migration and Reciprocal Displacement of Acid Groups in Acylated Dibromohydroxybenzylphenylhydrazines.** KARL AUWERS (*Ber.*, 1909, 42, 267—277).—An extension of the inquiry (*Abstr.*, 1908, i, 458). It has been shown that treatment of the dibromo- $\alpha$ -*N*-acetyl-*o*-benzoxybenzylphenylhydrazine,  $OBz \cdot C_6H_2Br_2 \cdot CH_2 \cdot N^{\alpha}Ac \cdot N^{\beta}HPh$ , with alcoholic potash does not yield the expected  $\alpha$ -*N*-acetate, but the  $\alpha$ -*N*-benzoate,



whether the hydrolysis is carried out with excess of alkali or not, or in the warm or in the cold. The *O*-radicle is usually the first to be split off, and this may then displace the acetyl group from its position, or the rule is reversed in this case, the *N*-acetyl being first hydrolysed with subsequent migration of the benzoyl group. It is, however, to be noted in this connexion that the *N*-acetates,  $\alpha$  and  $\beta$ , are very stable towards alkalis (10%), whereas the *NN*-diacetate and *NN*-triacetate give the  $\alpha$ -*N*-acetate with a 1% alcoholic solution of potassium hydroxide; further, one molecular equivalent of alkali with the triacetate does not give the *NN*-diacetyl compound—a portion of the compound is not attacked, the remainder being hydrolysed to  $\alpha$ -*N*-acetate.

With other esters the behaviour is quite otherwise, the *O*-propionyl- $\alpha$ -*N*-acetyl compound on partial hydrolysis with aniline gives  $\alpha$ -*N*-acetate and propionanilide; alcohol potassium hydroxide giving, however,  $\alpha$ -*N*-propionate and acetanilide. The *O*-acetyl- $\alpha$ -*N*-propionyl derivative is hydrolysed to  $\alpha$ -*N*-propionate in the normal manner.

The question of whether it is the greater mass of the migratory group which displaces the other acyl radicle, or whether it depends on the space occupied by the groups, was also examined, but the results so far obtained have been meagre. The reactivity of phenylhydrazine is largely decreased by the introduction of heavy acyl groups, and *s*-benzoyl or heptoylphenylhydrazide do not react with dibromo-*o*-hydroxybenzyl bromide or its esters under ordinary conditions. Indirect methods of preparing these  $\alpha$ -*N*-derivatives from phenylhydrazine and the corresponding ester of the bromide, whereby subsequent intramolecular change would be induced, have led to mixtures which could not be separated. The crude product, however, obtained by benzoylation of the  $\alpha$ -*N*-heptoate, on hydrolysis gave the  $\alpha$ -*N*-benzoate, so that it would appear that the heptoyl radicle containing the same number of carbon atoms as the benzoyl group is nevertheless displaced by it.

The formyl compounds are distinguished by the easy displacement

of the formyl group; thus the action of *s*-formylphenylhydrazide and dibromobenzyloxybenzyl bromide leads to the formation of the  $\alpha$ -*N*-benzoate, and an analogous result is obtained with the acetoxy-compound.

[With HUGO DANNEHL and K. MÜLLER.]—*s*-Phenyldibromo-*o*-hydroxybenzyl- $\alpha$ -*N*-formylhydrazine,  $C_{14}H_{12}O_2N_2Br_2$ , prepared by heating 2 mols. of *s*-formylphenylhydrazide with 1 mol. of dibromo-*o*-hydroxybenzyl bromide in benzene solution, crystallises from alcohol in colourless crystals, m. p. 164—165°. The  $\alpha$ -*N*-formyl-*O*- $\beta$ -*N*-diacetyl derivative,  $C_{18}H_{16}O_4N_2Br_2$ , is a yellow, amorphous powder, which on hydrolysis yields the  $\alpha$ -*N*-acetate. The *O*-benzoyl- $\alpha$ -*N*-formyl derivative,  $C_{21}H_{10}O_3N_2Br_2$ , crystallises from alcohol in very slender, white needles, m. p. 154° (decomp.). The *O*-acetyl- $\alpha$ -*N*-propionyl derivative,  $C_{18}H_{18}O_3N_2Br_2$ , crystallises from alcohol in glistening leaflets, m. p. 173—174°, and is not dissolved by aqueous alkali, showing that under these conditions migration of the acetyl group to the  $\beta$ -*N* does not occur. The  $\alpha$ -*N*-propionyl-*O*-benzoate,  $C_{23}H_{20}O_3N_2Br_2$ , forms colourless needles, m. p. 176—177°, and on hydrolysis yields the  $\alpha$ -*N*-benzoate.

The heptoate of dibromo-*o*-hydroxybenzyl bromide,  $C_{14}H_{17}O_2Br_2$ , prepared by heating the bromide with heptoyl chloride for three hours at 160°, crystallises from methyl alcohol in silken needles, m. p. 41°. The  $\alpha$ -*N*-heptoate forms slender needles, m. p. 146—148°, and is soluble in aqueous alkali. W. R.

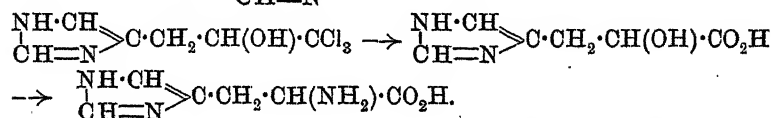
**Transformation of Azines into Hydrazones.** GUSTAV KNÖFFER (*Monatsh.*, 1909, 30, 29—38).—The results of the author's investigation of the behaviour of aldazines and ketazines towards phenylhydrazine show that all these azines are converted by this means into the corresponding hydrazones (compare Fulda, Abstr., 1903, i, 199; Ofner, Abstr., 1904, i, 818; Ott, Abstr., 1905, i, 376; Fürth, Abstr., 1907, i, 61). That the transformation, which takes place according to the equation:  $CHR:N:N:CHR + 2NHPPh \cdot NH_2 = 2CHR:N:NHPPh + N_2H_4$ , is not a consequence of the mass action of the reagent is shown by the fact that the reacting substances were taken in approximately theoretical proportions, the conversion of the azine being practically complete. The azine, suspended in alcohol (or acetic acid), was heated with phenylhydrazine in a reflux apparatus until complete solution occurred. The following azines of aldehydes and ketones giving azines and hydrazones which are readily identified were employed.

(1) Benzaldazine. (2) Salicylaldazine. (3) Anisalaldazine. (4) Cinnamaldazine. (5) Cuminalaldazine. (6) Furfuralaldazine. (7) *p*-Hydroxybenzaldazine. (8) Vanillaldazine. (9) Piperonalaldazine. (10) *p*-, (11) *o*-, and (12) *m*-nitrobenzaldazines. (13) *p*-Dimethylaminobenzaldazine. (14) Protocatechualdazine,  $C_{14}H_{12}O_4N_2$ , decomp. about 245°, which is readily soluble in alcohol. (15) Resorcyldaldazine,  $C_{14}H_{12}O_4N_2$ , which does not melt at 310°. (16) Methylphenylketazine. (17) Methyl-*m*-nitrophenylketazine,  $C_{16}H_{14}O_4N_4$ , m. p. 194—195°. (18) Methyl-*p*-aminophenylketazine,  $C_{16}H_{18}N_4$ , which forms heavy, yellow crystals, m. p. 166°, and dissolves readily in alcohol. (19) Benzylidenacetazine,  $C_{20}H_{20}N_2$ , which forms yellow crystals, m. p. 160°, and with phenyl-

hydrazine yields benzylideneacetonephenylhydrazine, m. p. 159° (Fischer, Abstr., 1884, 1150, found 157°). T. H. P.

**The Azoxine Analogue of apoSafranine.** FRIEDRICH KEHRMANN and WERNER GRESLY (*Ber.*, 1909, 42, 347—349).—The azoxine analogue of *aposafranine* and of *apothionine* has been prepared by eliminating an amino-group from diaminophenazonium chloride (Abstr., 1903, i, 279) in the usual way, and has been isolated as the dark red, crystalline *platinichloride*,  $(C_{12}H_9ON_2)_2PtCl_6$ . The *chloride* and impure *nitrate* have been prepared. C. S.

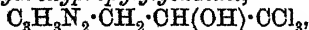
**Experiments on the Synthesis of Histidine.** OTTO GERNGROSS (*Ber.*, 1909, 42, 398—405).—The object of this investigation was the synthesis of histidine, which it was proposed to effect, starting from 4-methyliminazole (4-methylglyoxaline), by the following series of changes:

$$\begin{array}{c} \text{NH}\cdot\text{CH} \\ | \\ \text{CH}=\text{N} \end{array} \gg \text{CMe} + \text{CCl}_3\cdot\text{CHO} \rightarrow$$


The condensation product of 4-methylglyoxaline with chloral when hydrolysed with an aqueous alcoholic solution of sodium hydroxide yields, however,  $\alpha$ -methoxyglyoxaline-4-propionic acid, which has not yet been converted into histidine.

2-Methylquinoline and chloral when mixed form an *additive* product,  $C_{12}H_{10}ONCl_3\cdot H_2O$ , which crystallises in large, glistening cubes and prisms, sinters at 56°, m. p. 63°, and dissociates into its components when kept or when dissolved in water. 4-Methylglyoxaline and chloral form a similar *additive* product,  $C_6H_7ON_2Cl_3$ , which crystallises in rosettes of hexagonal plates, sinters at 116°, and has m. p. 123° (decomp.).

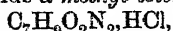
4- $\gamma\gamma\gamma$ -Trichloro- $\beta$ -hydroxypropylglyoxaline,



is prepared by heating 4-methylglyoxaline with chloral for forty-two hours at 78—80°; it crystallises in prisms, m. p. 195° (decomp.); the *hydrochloride*,  $C_6H_5ON_2Cl_4$ , forms stellate groups of crystals, and decomposes between 230—260°; the *nitrate* forms large, colourless, glistening prisms, decomposing above 195°; the *oxalate* forms rosettes of prisms. The base is converted by sodium hydroxide in aqueous methyl alcohol at 25° into  $\alpha$ -methoxyglyoxaline-4-propionic acid, which crystallises in rectangular plates, turns yellow at 210°, and decomposes at 221°; the *hydrochloride*,  $C_7H_{10}O_3N_2\cdot HCl$ , forms small needles, sinters at 170°, and decomposes at 172°. The *methyl ester hydrochloride*,  $C_8H_{12}O_3N_2\cdot HCl$ , prepared by the action of hydrogen chloride on a solution of the acid in methyl alcohol, forms silky needles, which become orange-yellow at 173° and have m. p. 185° (decomp.).

$\alpha$ -Chloroglyoxaline-4-propionic acid, prepared from histidine by the

method of Windaus and Vogt (*Beitr. chem. Physiol. Path.*, 1907, 9, 406), has m. p. 191° and yields a *methyl ester hydrochloride*,



crystallising in large, thin, glistening plates, m. p. 140°. W. H. G.

**Isatoic Anhydride (Anthranilcarboxylic Acid).** ERNST MOHR (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 96—97).—Isatoic anhydride dissolves in an excess of cold sodium or barium hydroxide; the clear solution yields sodium or barium carbonate and anthranilate when boiled. Isatoic anhydride dissolves in water containing an equal molecular quantity of sodium hydroxide, forming a solution

which probably contains the sodium derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}-\text{O} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{Na} \quad \text{CO} \end{smallmatrix}$  or  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}-\text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C} \cdot \text{ONa} \end{smallmatrix}$ , precipitates a corresponding barium derivative on

the addition of barium chloride, and regenerates isatoic anhydride when acidified. After a short time, the solution deposits isatoic anhydride, and under certain conditions contains sodium anthranoyl-anthranilate, due to the action of the anhydride or its sodium derivative on the sodium anthranilate produced. Similarly, isatoic anhydride reacts with glycine to form *o*-aminohippuric acid. C. S.

**Action of Hydriodic Acid and of Iodine on Dimethylamino-antipyrine (Pyramidone).** HENRI COUSIN (*Bull. Soc. chim.*, 1909, [vi], 5, 121—124; *J. Pharm. Chim.*, 1909, [vi], 29, 49—54).—Hydriodic acid acts on pyramidone, forming the *iodide*,  $\text{C}_{13}\text{H}_{17}\text{ON}_3\text{HI}$ , colourless prisms, m. p., indistinct, above 200° (decomp.). When iodine is added to this salt, or to the free base in alcoholic solution, the *periodide*,  $\text{C}_{13}\text{H}_{17}\text{ON}_3\text{HI}_2$ , is obtained as brown needles insoluble in water. G. B.

**5-Amino-1-phenyl-3-methylpyrazole.** ERNST MOHR [and, in part, LUDWIG SCHMIDT] (*J. pr. Chem.*, 1909, [ii], 79, 1—49).—A continuation of the researches of von Walther (Abstr., 1897, i, 297). Many of the compounds described in this paper have already been investigated (compare Michaelis, Abstr., 1905, i, 476; Michaelis and Klopstock, Abstr., 1907, i, 735). The cyanoacetonephenylhydrazone, prepared by the interaction of  $\beta$ -aminocrotononitrile and phenylhydrazine in dilute acetic acid, has m. p. 99—100° (compare Burns, Abstr., 1893, i, 314; von Walther, *loc. cit.*). The product obtained when the two substances are heated together, or in alcoholic solution, has m. p. 88—94°, and dissolves in cold concentrated sulphuric acid, forming an intense blood-red solution; the substance m. p. 99—100° does not give an intense coloration; these differences cannot yet be explained. Both substances when warmed with dilute hydrochloric acid at about 55° yield 5-amino-1-phenyl-3-methylpyrazole. The latter compound appears to react both

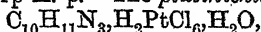
as an iminopyrazolone,  $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{NPh} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$ , and as an aminopyrazole,  $\text{N} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{NPh} \cdot \text{C} \cdot \text{NH}_2 \end{smallmatrix}$ , for when it is treated with sodium nitrite and

dilute hydrochloric acid it yields 4-oximino-5-imino-1-phenyl-3-methylpyrazolone (compare von Walther, *loc. cit.*) and 5-diazo-1-phenyl-3-methylpyrazole chloride; the presence of the latter in the solution is shown by the formation of an azo-dye on the addition of an alkaline solution of  $\beta$ -naphthol.

4-Oximino-5-imino-1-phenyl-3-methylpyrazolone appears to behave as a tautomeric substance, represented by the formulæ  $N \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{NO} \\ \text{NPh} \cdot \text{C} \cdot \text{NH}_2 \end{smallmatrix}$

and  $N \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{N} \cdot \text{OH} \\ \text{NPh} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$ ; thus it reacts both as an acid and as a base; the solid substance is bright red, the molten substance is dark green; the dilute solutions in indifferent solvents are sky-blue, the alcoholic solution is reddish-violet.

5-Amino-1-phenyl-3-methylpyrazole hydrochloride, when crystallised from hot dilute hydrochloric acid, forms long, white needles; it contains water and hydrogen chloride in a loose state of combination, and does not give a sharp m. p. The *platinichloride*,



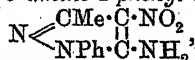
crystallises in slender, reddish-yellow needles, m. p. 169°, which when kept in the mother liquor change into compact, orange-red prisms, m. p. 176–178° (decomp.).

1-Phenyl-3-methylpyrazole-5-azo- $\beta$ -naphthol,  $\text{C}_{20}\text{H}_{16}\text{ON}_4$ , crystallises in glistening, bright red, microscopic needles, m. p. 209–210°.

During the preparation of 4-oximino-5-imino-1-phenyl-3-methylpyrazolone, a by-product was obtained, which is possibly 5-imino-1-phenyl-3-methyl-4:5-pyrazoquinone,  $N \begin{smallmatrix} \text{CMe} \cdot \text{CO} \\ \text{NPh} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$ ; it crystallises in aggregates of lemon-yellow needles, m. p. 133–134°.

4:5-Diamino-1-phenyl-3-methylpyrazole condenses with benzil, yielding triphenylmethylpyrazopyrazine,  $N \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{N} \cdot \text{CPh} \\ \text{NPh} \cdot \text{C} \cdot \text{N} \cdot \text{CPh} \end{smallmatrix}$ , which crystallises in very pale lemon-yellow needles, m. p. 190°.

4-Oximino-5-imino-1-phenyl-3-methylpyrazolone is converted by an alkaline solution of potassium hypochlorite into 1-phenyl-3-methyl-4:5-pyrazoquinonedioxime anhydride,  $N \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{N} \\ \text{NPh} \cdot \text{C} \cdot \text{N} \end{smallmatrix} > \text{O}$ , straw-yellow plates, m. p. 94–95°, and by potassium permanganate in dilute sulphuric acid into 4-nitro-5-amino-1-phenyl-3-methylpyrazole,



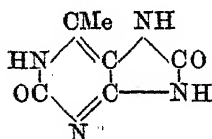
a yellowish-brown powder, m. p. 167–168°.

W. H. G.

**Pyrimidines. XLI. Formation of Purine Derivatives from 4-Methylcytosine.** CARL O. JOHNS (*Amer. Chem. J.*, 1909, 41, 58–65. Compare Abstr., 1908, i, 917).—When 2-oxy-6-amino-4-methylpyrimidine (4-methylcytosine) is nitrated in presence of sulphuric acid, an almost quantitative yield of 5-nitro-4-methylcytosine,  $N \begin{smallmatrix} \text{CO} & \text{NH} \\ \text{C}(\text{NH}_2) \cdot & \text{C}(\text{NO}_2) \end{smallmatrix} > \text{CMe}$ , is obtained; it crystallises from water in

small, yellow prisms, decomp. 260—280°. The position of the nitro-group is shown by the formation of Behrend's 5-nitro-4-methyluracil when it is heated with 30% sulphuric acid in a sealed tube. When treated in a similar manner with 20% acid, cytosine and nitrocytosine give respectively uracil and nitrouracil. Attempted reduction of 5-nitro-4-methylcytosine by means of ammonium sulphide regenerated 4-methylcytosine, but aluminium amalgam reduces it to 5:6-diamino-

2-oxy-4-methylpyrimidine,  $\text{N} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{NH}_2) \cdot \text{C}(\text{NH}_2) \end{array} \text{NH} \rangle \text{CMe}$ , crystallising

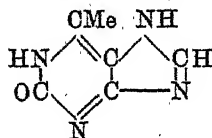


from water in long prisms containing 1 mol.  $\text{H}_2\text{O}$ , which do not melt, but decomp. at 280—285°; the picrate, decomp. 240°.

5:6-Diamino-2-oxy-4-methylpyrimidine condenses with carbamide when the anhydrous substances are heated together at 170—180°, giving 2:8-dioxy-6-methylpurine (annexed formula),

forming small, sparingly soluble crystals that do not melt below 345°.

This compound is the last of the three possible dioxypurines to be prepared. In a similar manner, by condensing with thiocarbamide, 2-oxy-8-thio-6-methylpurine is obtained; it is an almost insoluble, crystalline powder, not melting below 345°.



5:6-Diamino-2-oxy-4-methylpyrimidine when heated with formic acid yields the *monoformyl* compound,  $\text{C}_5\text{H}_7\text{ON}_4\text{CHO}$ , which forms minute crystals from hot water solutions, not melting below 345°. This substance gives a white, crystalline sodium salt, which loses water vigorously at 200°, leaving a porous mass, 2-oxy-6-methyl-

purine (annexed formula), readily soluble in water, crystallising therefrom in slender prisms, not melting, but decomp. at 300—345°.

J. V. E.

**Synthesis of 1-Methylxanthine.** MAX ENGELMANN (*Ber.*, 1909, 42, 177—182).—1-Methylxanthine was first isolated from human urine by Krüger and Salomon (*Abstr.*, 1898, i, 699). Since it had not been synthesised hitherto, the author has effected this, starting from cyanamide and methyl alcohol. Methylisocarbamide (methyl imino-carbimate), prepared from cyanamide and methyl alcohol (compare Stieglitz and McKee, *Abstr.*, 1900, i, 340), condenses with ethyl cyanoacetate in the presence of sodium ethoxide, forming 4-imino-6-oxy-2-methoxydihydropyrimidine,  $\text{NH} \begin{array}{c} \text{C}(\text{OMe})\text{N} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{CH}_2 \end{array} \rangle \text{C:NH}$ , a crystalline substance, m. p. 214—216°, which, when treated with methyl sulphate and aqueous sodium hydroxide, yields 4-imino-6-oxy-2-methoxy-1-methyldihydropyrimidine,  $\text{C}_6\text{H}_9\text{O}_2\text{N}_3$ , colourless crystals, m. p. 206—208°. The latter substance is converted by sodium nitrite and acetic acid into 5-oximino-4-imino-6-oxy-2-methoxy-1-methyldihydropyrimidine, small, violet needles, m. p. about 145° (decomp.), which, when reduced with ammonium sulphide, yields 4:5-diamino-6-oxy-2-methoxy-1-methylpyrimidine, crystallising in needles, m. p. 160°. The latter substance is converted by hot concentrated hydrochloric acid

into 4:5-diamino-2:6-dioxy-1-methylpyrimidine, the hydrochloride of which, when heated with sodium formate and formic acid at  $100^{\circ}$ , yields 5-formylamino-4-amino-2:6-dioxy-1-methylpyrimidine, crystallising in needles which do not melt at  $300^{\circ}$ ; the crystalline sodium salt, when heated at  $230-240^{\circ}$ , liberates  $1\text{H}_2\text{O}$ , with the formation of 1-methyl-xanthine.

W. H. G.

**Action of Unsymmetrical Benzoylphenylhydrazine on o-Benzoquinone.** WILLIAM MCPHERSON and H. J. LUCAS (*J. Amer. Chem. Soc.*, 1909, 31, 281—284).—It has been shown in earlier papers (Abstr., 1896, i, 127; 1900, i, 411; 1901, i, 572) that unsymmetrical acylphenylhydrazines react with *p*-benzoquinone to form hydrazones of the general formula  $\text{O}:\text{R}:\text{N}:\text{N}:\text{AcR}'$ . Willstätter and Veraguth (Abstr., 1907, i, 453) have found that, under certain conditions, these hydrazones readily undergo a rearrangement into the isomeric hydroxyazo-compounds,  $\text{OAc}:\text{R}:\text{N}:\text{N}:\text{NR}'$ , in which the acyl group is attached to the oxygen atom.

By the action of  $\alpha$ -benzoylphenylhydrazine on *o*-benzoquinone, *o*-benzoxazobenzene,  $\text{OBz}:\text{C}_6\text{H}_4:\text{N}:\text{N}:\text{Ph}$ , is produced. It is probable that in this reaction the hydrazone,  $\text{O}:\text{C}_6\text{H}_4:\text{N}:\text{NBzPh}$ , is formed first, and instantly undergoes rearrangement. *o*-Benzoxazobenzene, m. p.  $93^{\circ}$ , crystallises in orange needles or plates, and on hydrolysis yields *o*-hydroxyazobenzene (Bamberger, Abstr., 1900, i, 531), which on benzoylation is re-converted in the original substance.

$\alpha$ -Benzoylphenylhydrazine reacts with tetrachloro-*o*-quinone with formation of the compound  $\text{C}_6\text{Cl}_3\text{O}_2:\text{NH}:\text{NBzPh}$ .

E. G.

**Mechanism of Coupling Reactions.** HANS TH. BUCHERER (*Ber.*, 1909, 42, 47—49. Compare Dimroth and Hartmann, this vol., i, 66).—The author and Sonnenburg have found that 2-naphthol-1-sulphonic acid couples with diazotised *p*-nitroaniline in sodium acetate solution to form *p*-nitrobenzene-azo- $\beta$ -naphthol, whilst in sodium carbonate solution the product of coupling is an easily soluble substance, which readily changes to the preceding compound, and is regarded as an *O*-azo-derivative,  $\text{SO}_3\text{Na}:\text{C}_{10}\text{H}_6:\text{O}:\text{N}_2:\text{C}_6\text{H}_4:\text{NO}_2$ .

*O*-Azo-compounds have also been obtained from  $\alpha$ -naphthol-6:8-disulphonic acid or salicylic acid and diazotised naphthionic acid or diazotised aniline; these compounds readily change to ordinary *o*- or *p*-hydroxyazo-compounds.

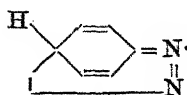
C. S.

**Decomposition of Diazo-solutions.** CARL G. SCHWALBE (*Ber.*, 1909, 42, 196—199. Compare Abstr., 1905, i, 618, 843).—Polemical. Mainly a reply to Cain (this vol., i, 70). Emphasis is laid on the fact that the author studied the rates of decomposition of diazo-solutions as prepared technically. The quantity of nitrous acid present in such solutions is sufficient to produce an increase in the velocity of decomposition.

W. H. G.

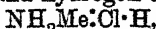
**Cain's Theory of Diazonium and Ammonium Salts.** ARTHUR HANTZSCH (*Ber.*, 1909, 42, 394—398. Compare Abstr., 1908, i, 1021).—Polemical. [A further reply to Cain (this vol., i, 70). The chief

points raised are as follows: (1) Comparison of the instability of the  $C_6$ -ring in benzoquinone towards halogens, hydrogen chloride, mild oxidising agents, etc., with the stability of the benzene nucleus in diazonium salts towards these reagents, shows that these two classes of compounds do not contain the same  $C_6$ -ring as represented by Cain's formula; (2) contrary to Cain's statement, the double linking in the group  $-N:N-$  is readily resolved by mild reducing agents, as



in the conversion of azobenzene into hydrazobenzene. A compound having the annexed formula would yield on reduction a diamine and not phenylhydrazine, since the nitrogen atom in the group  $\begin{matrix} H \\ N > C < C \\ N & & C \end{matrix}$  would not be separated from

the carbon atom by mild reducing agents; (3) it does not necessarily follow from the non-existence of aliphatic diazonium salts that the presence of the benzene nucleus is essential for the formation of diazonium salts. The stability of the latter is greatly influenced by substitution in the benzene ring, and it is not remarkable that the compound resulting from the total replacement of the benzene nucleus by an alkyl group decomposes spontaneously; (4) the process of ionisation of ammonium salts in the manner represented by Cain is very improbable, since in the case of trimethylethylammonium hydroxide and the corresponding nitrate, dissociated ethyl alcohol and ethyl nitrate would be formed intermediately; ethyl nitrate does not, however, form ions. Further, if the addition of alkyl halides to amines takes place thus:  $R_3N + ClR \rightarrow R_3N:Cl \cdot R$ , then the compound formed from methylamine and hydrogen chloride, namely,



should be isomeric with that derived from ammonia and methyl chloride, namely,  $NH_3:Cl \cdot Me$ . W. H. G.

**Change of Colour in Additive Reactions.** DANIEL VORLÄNDER (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1907, ii, 91).—The salts of aminoazo-compounds and acids may be regarded as additive compounds or as ammonium salts. If the latter is correct, azobenzene-trimethylammonium chloride should be red; this is not the case, the azo-ammonium ion being orange-yellow, like azobenzene and aminoazobenzene.

Solutions of hydrogen chloride or bromide in benzene, carbon tetrachloride, or chloroform immediately colour dimethylaminoazobenzene. Moreover, dimethylaminoazobenzene and *p*-methoxydimethylaminoazobenzene form dark red, conducting solutions in dry, liquid sulphur dioxide, whereas the solution of aminoazobenzene is yellow and non-conducting. An additive compound with sulphur dioxide is probably formed in the former, but not in the latter, case. The author draws the conclusion that the colour of the compounds of aminoazobenzenes and acids is conditioned by an additive relation between the amine and the acid. The cause of the different colour of the acid derivatives and of the quaternary ammonium salts is attributed to the fact that, in the former, the union of the constituents is loose and of the nature

of that of a double salt, whilst in the case of the ammonium derivatives the constituents are more intimately united, as in complex salts.  
C. S.

**Study of the Constitution of Proteins by the Hydrolytic Action of Hydrogen Fluoride.** Preparation of Definite Natural Peptides. LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1909, 148, 236—238. Compare Abstr., 1908, i, 706).—The author has extended his experiments on the use of hydrogen fluoride in the hydrolysis of proteins. The 60% acid diluted with twice its volume of water effects the complete hydrolysis of gelatin with production of free amino-acids. More dilute acid, however, is incapable of bringing about such profound decomposition; the products in this case consist of diamines and certain uncrystallisable polypeptides, which have been isolated in the form of well-defined picrates, and are analogous to some synthetic polypeptides described by Fischer (Abstr., 1906, i, 73). They appear to exist in proteins in definite combination, and not to have arisen through the synthetic action of the hydrogen fluoride.

The following compounds have been isolated from the products of hydrolysis of pepsin extract. *Arginyl-arginine dipicrate*,

$C_{18}H_{38}O_4N_{12} \cdot (C_6H_5O_7N_3)_2 \cdot 2H_2O$ ,  
m. p. 207° (corr.). *Glutamin-lysine picrate*,  $C_{11}H_{21}O_5N_2 \cdot C_6H_5N_3O_7 \cdot H_2O$ ,  
prisms, m. p. 216°. *Lysyl-lysine dipicrate*,  $C_{12}H_{26}O_3N_4 \cdot (C_6H_5O_7N_3)_2$ ,  
small tablets, m. p. 238—242°.

From gelatin, *arginyl-arginine picrate*,  $C_{12}H_{26}O_3N_4 \cdot C_6H_5O_7N_3 \cdot 2H_2O$ ,  
has been prepared. It forms needles, m. p. 213°. W. O. W.

**Combining Power of Egg-white for Hydrochloric and Sulphuric Acids.** HERBERT E. ROAF (*Proc. physiol. Soc.*, 1908, iv; *J. Physiol.*, 38).—Diluted egg-white was placed in a series of dialysing tubes immersed in various strengths of acid. After some days the amount of acid in the outer vessel was estimated, and it was found that with two acids (sulphuric and hydrochloric) and varying concentrations, equivalent amounts are taken up by the same quantity of protein. It was to be expected that proteins as complex amino-acids should show a definite combining power for acids and alkalis.

W. D. H.

**Osmotic Pressure of Hæmoglobin.** HERBERT E. ROAF (*Proc. physiol. Soc.*, 1908, i—ii; *J. Physiol.*, 38).—The experiments were made by laking red corpuscles of the cow, freed from serum, with water. The hæmoglobin was reckoned as 90% of the dry organic matter. Their object was to determine the effect of altered conditions on the "solution aggregate" of the hæmoglobin. Three determinations of osmotic pressure were made: (1) with distilled water, (2) with 0.34% sodium hydrogen carbonate, and (3) with 0.2% of sodium carbonate; the results for 1% of hæmoglobin were 5.7, 5.3, and 11.6 mm. of mercury respectively, which correspond with "aggregates" of 29787, 32035, and 14636 respectively. The osmotic pressure of protein solutions is altered by electrolytes and non-

electrolytes. Substances which prevent laking lower the osmotic pressure of hæmoglobin; hæmoglobin is more affected by electrolytes than are serum-proteins. It is possible that the osmotic changes which occur in muscular contraction may be due to alterations in the aggregation of proteins and not to liberation of inorganic salts.

W. D. H.

**Nucleo-protein of the Pig's Liver.** VITTORIO SCAFFIDI (*Zeitsch. physiol. Chem.*, 1909, 58, 272—281).—By boiling and precipitation with acetic or tartaric acid, a nucleo-protein was obtained from pig's liver which contains 3.48—3.73% of purine nitrogen, 2.67% of phosphorus, and a pentose. It also contains iron in quantities varying from 0.5 to 3.6%. Schmiedeberg's ferratin, which was prepared in much the same way, contained 6% of iron. W. D. H.

**Action of Rennet at Various Temperatures.** C. GERBER (*Compt. rend.*, 1908, 147, 1320—1322).—There are many causes which produce deviations from the law, that the times taken to curdle a given quantity of milk are inversely proportional to the amount of ferment added. The present paper is concerned with such deviations as are due to a too speedy curdling, so that the product of time and quantity of ferment is lowered. These deviations increase with the temperature, and at the same temperature they increase with the quantity of ferment added. For the same quantity of rennet, they are largest with specimens of rennet containing a high proportion of saline constituents. Calcium chloride, however (and to some extent, hydrochloric acid), has an accelerating effect which is greatest when the enzyme concentration is greatest, so that the above-mentioned negative deviation, due to the large quantity of ferment present, is annulled; the process thus becomes regular, and the law is followed. G. B.

**A New Artificial Peroxydase.** E. DE STOELIN (*Compt. rend.*, 1908, 147, 1489—1491. Compare Abstr., 1908, i, 490, 746; ii, 573).—Iron tannate can act as a peroxydase, and in conjunction with hydrogen peroxide oxidises a number of substances which are resistant to all peroxydases hitherto known. In particular, it attacks substances containing a single phenolic hydroxyl, for instance, guaiacol. It acts like a true enzyme, oxidising many times its own weight of ethyl alcohol to acetaldehyde, and it produces a black substance from tyrosine in the same way as tyrosinase. G. B.

[**Effect of Adsorbents on Yeast Juice.**] LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1908, 15, 217—219).—In reference to Resenscheck's work (this vol., i, 74), the authors state that they also find that the presence of negative adsorbents diminishes the fermentative capacity of yeast juice to a small extent. Positive adsorbents have a somewhat greater inhibitory influence. S. B. S.

## Organic Chemistry.

The Relative Ease of Addition in the Alkylene Group. ARTHUR MICHAEL and ROGER F. BRUNEL (*Amer. Chem. J.*, 1909, 41, 118—148).—Exceptions to Markownikoff's rule governing the addition of halogen acids to unsaturated hydrocarbons have been indicated by Saytzeff (*Annalen*, 1875, 179, 296) and Linnemann (*Annalen*, 1872, 163, 96). In a series of papers (Abstr., 1888, 1054; 1900, i, 321; 1904, ii, 164; 1906, i, 550, 551), Michael has developed the view that a general law of addition connecting the course of the process with the structure of the substances can be based on the "positive-negative" hypothesis. This positive-negative law of addition is supported by the work of Berthelot (*Compt. rend.*, 1862, 54, 1350) and Butleroff (*Annalen*, 1875, 180, 246; *Ber.*, 1873, 6, 561) on ethylene, propylene, and isobutylene, whilst the observations of Butleroff (*Annalen*, 1877, 189, 51; Abstr., 1880, 230) and Kondakoff (Abstr., 1897, i, 177) tend to confirm the existence of a maximum additive power in the series, deduced theoretically.

In order to determine where this maximum occurs, the behaviour of the butylenes,  $\beta$ -methyl- $\Delta^{\beta}$ -butylene,  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene, and diisobutylene, towards sulphuric acid of different strengths, the halogen acids, and phosphoric acid has been studied.

At 28—29° a mixture of 1.5 parts of sulphuric acid with 1 part of water absorbs isobutylene about twelve times as fast as  $\psi$ -butylene, which is absorbed by (5:1) sulphuric acid at about the same rate as the isobutylene is absorbed by the weaker acid. At the same temperature  $\psi$ -butylene is absorbed almost twice as fast as  $n$ -butylene by sulphuric acid of the strength 3.5:1.

When isobutyl alcohol is dehydrated by passing its vapour through a Jena combustion tube containing pieces of a graphite crucible heated at 500°, analysis of the gas produced, by absorption with sulphuric acid shows that it contains 55% of isobutylene and 2.5—3.0% of a gas unabsorbed by bromine, whilst if the graphite is replaced by aluminium oxide, the evolved gas contains 65—70% of isobutylene and about 1% of hydrogen.

isoButylene is dissolved by sulphuric, phosphoric, and hydrochloric acids at least three times as fast as  $\beta$ -methyl- $\Delta^{\beta}$ -butylene, whilst the latter is absorbed twelve times as rapidly as  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene by (2:1) sulphuric acid. Although  $\beta\gamma$ -dimethyl- $\Delta$ -butylene dissolves readily in sulphuric acid of the strength 4:1, diisobutylene is not dissolved, but is polymerised by twelve days' contact with this acid.

Thus it is found that of all the alkynes examined, isobutylene has the greatest additive power, the expected decrease occurring between this hydrocarbon and  $\beta$ -methyl- $\Delta^{\beta}$ -butylene. Moreover, as predicted by theory, the difference in additive power between  $\beta$ -methyl- $\Delta^{\beta}$ -butylene and  $\beta\gamma$ -dimethyl- $\Delta^{\beta}$ -butylene is much greater than that between isobutylene and the former hydrocarbon.

E. H.

**Comparative Stability of Bromoform, Chloroform, and Iodoform.** WILLIAM OECHSNER DE CONINCK (*Rev. gén. Chim. pure et appl.*, 1909, 12, 81).—Bromoform or chloroform when distilled from lead nitrate alone, or from an aqueous alcoholic solution of this salt, shows no signs of decomposition. When iodoform is thus treated, the following reaction occurs:  $2\text{Pb}(\text{NO}_3)_2 + 2\text{CHI}_3 + \text{O} = 2\text{PbI}_2 + \text{I}_2 + 2\text{CO}_2 + \text{H}_2\text{O} + 2\text{H}_2\text{O}$ . This change takes place with the dry materials, but in alcoholic solution at  $94^\circ$  no decomposition is observed.

G. T. M.

**Preparation of Acetylene Di- and Tetra-chlorides from Acetylene and Chlorine.** J. H. LIDHOLM (D.R.-P. 204516).—The interaction of chlorine and acetylene may be controlled by employing a definite source of light, such as a quartz-mercury lamp actuated by a current of 5 amperes and 60–75 volts. A mixture of two volumes of chlorine and one of acetylene when thus illuminated reacts quite quietly, yielding chiefly acetylene tetrachloride with about 10% of the dichloride.

G. T. M.

**Preparation of Trimethylene Chlorobromide and Dibromide.** PIERRE BRUYLANTS (*Bull. Acad. roy. Belg.*, 1908, 1085–1094).—The cyclopropanecarboxylonitrile required for the preparation of the compounds described elsewhere (this vol., i, 226) was obtained by treating  $\gamma$ -chlorobutyronitrile with dry potassium hydroxide, and this compound was prepared by Henry's method, the action of potassium cyanide on trimethylene chlorobromide. The author found the methods described by Reboul (*Abstr.*, 1879, 127) and by Lermantoff (*Abstr.*, 1877, 59) for the preparation of trimethylene chlorobromide ( $\alpha$ -chloro- $\gamma$ -bromopropane) unsatisfactory; the following modification of the process, however, gave a satisfactory yield of the product, and did not involve the use of sealed tubes. Allyl chloride is saturated with moist hydrogen bromide at  $20$ – $22^\circ$  in sunlight, and the operation repeated until the gas ceases to be absorbed. Trimethylene dibromide ( $\alpha\gamma$ -dibromopropane) is similarly prepared from allyl bromide and hydrogen bromide at  $30$ – $35^\circ$ .

M. A. W.

**Preparation of Nitromethane.** ANDRÉ WAHL (*Bull. Soc. chim.*, 1909, [iv], 5, 180–182. Compare Freibisch, this Journ., 1874, 462; Auger, *Abstr.*, 1900, i, 578, and Steinkopf, this vol., i, 78).—A solution of 100 grams of monochloroacetic acid in 100 c.c. of water is neutralised with a solution of sodium carbonate (90 grams in 150 c.c. of water), and to this is added 90 grams of sodium nitrite. The solution is warmed, gently at first, and when the reaction has set in, a current of steam is passed through and about 175 to 190 c.c. of distillate is collected. The nitromethane is decanted, and that contained in the decantation liquid is recovered by a second distillation. The yield is about 50% of the theoretical.

T. A. H.

**Oxidation of Alcohols by Simultaneous Action of Ferrous Tannate and Hydrogen Peroxide.** E. DE STOELIN (*Compt. rend.*, 1909, 148, 424–426. Compare this vol., i, 196).—The author has

studied quantitatively the oxidation of ethyl alcohol by hydrogen peroxide in presence of ferrous tannate, and gives tables showing the amount of aldehyde and acetic acid formed when 50% alcohol, and also when acetaldehyde, is submitted to oxidation in presence of varying amounts of the iron salt. The results lead to the following conclusions: (1) the alcohol is first converted into aldehyde, (2) the aldehyde undergoes further oxidation to acetic acid, (3) a portion of the aldehyde is absorbed by the ferrous tannate, (4) part of the aldehyde is probably converted into an aldehyde peroxide, (5) the amount of aldehyde and acetic acid formed increases with the weight of iron present.

It has been observed that oxidation takes place when other organic compounds are substituted for tannin in these experiments.

Methyl, ethyl, *n*-propyl, and *n*-butyl alcohols have been oxidised in the same way, but isopropyl and isobutyl alcohols, the higher alcohols, and also polyhydric alcohols, such as glycol, glycerol, and sorbitol, resist attack.

W. Q. W.

**Catalytic Action of Coal, Brown Coal, or Peat in the Aerial Oxidation of Organic Substances.** MAX DENNSTEDT and F. HASSLER (D.R.-P. 203848).—The oxidation of many organic substances can be brought about by passing their vapours mixed with air over coal heated at 150–300°. In this way ethyl alcohol is oxidised to acetaldehyde and acetic acid, toluene to benzaldehyde and benzoic acid, naphthalene to naphthaquinone and phthalic anhydride, anthracene to anthraquinone, and borneol or isoborneol to camphor and camphoric acid. Brown coal and peat have a similar effect, which appears to be due to the contained iron. Accordingly, ferruginous compounds are added when the amount of iron originally present in the coal or peat is only small.

G. T. M.

**Action of Ethyl Mesoxalate on Alkyl Magnesium Halides and the Synthesis of  $\beta\delta$ -Dimethylpentane- $\beta\delta$ -diol.** JOSEPH LEMAIRE (*Bull. Acad. roy. Belg.*, 1909, 83–159).—The primary object of the research described was the preparation of pentamethylglycerol,  $\text{OH}\cdot\text{CMe}(\text{CMe}_2\cdot\text{OH})_2$ , and the first method tried was the action of Grignard's reagent on ethyl mesoxalate. The latter was prepared by a modification of the method described by Curtis (Abstr., 1906, i, 480). As Wieland (Abstr., 1904, i, 596) by the action of dry nitrous anhydride on  $\alpha\gamma$ -diphenylpropane- $\alpha\gamma$ -dione has obtained the definite intermediate compound,  $\text{N}_2\text{O}_2[\text{CH}(\text{COPh})_2]_2$ , which is decomposed by dilute sulphuric acid, giving  $\alpha\gamma$ -diphenylpropanetrione,  $\text{COPh}\cdot\text{CO}\cdot\text{COPh}$ , it is suggested that in Curtis's reaction an analogous compound,  $\text{N}_2\text{O}_2[\text{CH}(\text{CO}_2\text{Et})_2]_2$ , is formed and decomposed by the water contained in the nitrous anhydride. When ethyl mesoxalate (1 mol.) is treated with magnesium methyl bromide (5 mols.), dihydroxytetramethylacetone,  $\text{CO}(\text{CMe}_2\cdot\text{OH})_2$ , small crystals, m. p. 117–118°, b. p. 238–240°/755 mm., is formed, the medial carbonyl group remaining unattacked. The latter observation, taken in conjunction with the fact that the medial carbonyl group in triketopentane is also stable towards Grignard's reagent, indicates that this inactivity is due in both cases

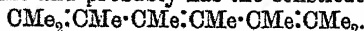
to the negative influence of the neighbouring groups. Dihydroxy-tetramethylacetone does not form a phenylhydrazone or a semicarbazone, and does not combine with hydrogen cyanide. The conclusion is drawn that the activity of the carbonyl group is inhibited by the two adjacent tertiary hydroxyl groups. Moreover, since the latter are attacked by phosphorus pentachloride and sulphuryl chloride, but not by acetyl and benzoyl chlorides, the behaviour of the complex  $\text{:C(OH)·CO·C(OH):}$  seems comparable with that of the carboxyl group.

Ethyl magnesium bromide (5 mols.) in ethereal solution acts on ethyl mesoxalate, giving a mixture of four substances. The chief product consists of *ethyl hydroxydiethylpyruvate*,  $\text{OH·CET}_2\text{·CO·CO}_2\text{Et}$ , a greenish-yellow liquid, b. p. 230—232°,  $D^{20}$  1.037,  $n_D$  1.44335, which does not solidify at  $-60^\circ$  and does not react with phenylhydrazine or semicarbazide. The second compound is a pale green *liquid*,  $\text{C}_6\text{H}_{11}\text{O}_2$ , b. p. 140—150°/755 mm., having an agreeable odour. The third product is a golden-yellow *liquid*,  $\text{C}_7\text{H}_{10}\text{O}_3$ , b. p. 199—200°/750 mm., which forms a *semicarbazone*, m. p. 142°. The quantity obtained of the fourth substance was insufficient for identification, but it seems to be dihydroxytetraethylacetone. The conclusion is drawn that ethyl magnesium halides are more active towards ethyl mesoxalate than methyl compounds, and that the bad yield of dihydroxytetramethylacetone, when using the latter, is due to the formation of ethyl hydroxydimethylpyruvate.

Magnesium propyl bromide reacts similarly to the ethyl compound with ethyl mesoxalate.

The production of dihydroxytetramethylacetone rendered the preparation of  $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol desirable for purposes of comparison. Attempts to prepare this compound by the action of methyl magnesium bromide on acetylacetone, ethyl malonate, ethyl chloromalonate, ethyl acetoacetate, ethyl sodioacetoacetate, or malonyl chloride were unsuccessful.

Ethyl  $\beta$ -chloroisovalerate (1 mol.), prepared in the manner described by Montemartini (Abstr., 1898, i, 236), reacts with methyl magnesium bromide (2 mols.) giving (1) a *liquid*, b. p. 126—128°, with a camphor-like odour, which combines readily with bromine and must be either  $\text{CMe}_2\text{Cl·CH}_2\text{·CMe·CH}_2$  or  $\text{CMe}_2\text{·CH·CMe}_2\text{Cl}$ , and (2) a liquid which is probably a mixture of the above compound and its parent chlorohydrin,  $\text{CMe}_2\text{Cl·CH}_2\text{·CMe}_2\text{·OH}$ . An attempt to prepare the unsaturated chlorohydrin having the second of the above two formulæ by the action of hydrogen chloride on Grignard's tetramethylallyl alcohol,  $\text{CMe}_2\text{·CH·CMe}_2\text{·OH}$ , gave a mixture of  $\beta\delta$ -dimethyl- $\Delta^{\beta\gamma}$ -pentadiene,  $\text{CMe}_2\text{·C·CMe}_2$ , and a *dipolymeride* of the latter, a liquid,  $\text{C}_{14}\text{H}_{24}$ , b. p. 215°/755 mm.,  $D^{20}$  0.8533,  $n_D$  1.4838, which combines with 3 molecules of bromine and probably has the constitution



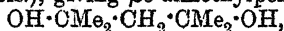
Since the latter hydrocarbon probably results from the condensation of 2 molecules of  $\delta$ -chloro- $\beta\delta$ -dimethyl- $\Delta^{\beta}$ -pentene,  $\text{CMe}_2\text{Cl·CH·CMe}_2$ , with elimination of hydrogen chloride, whilst the unsaturated chlorohydrin obtained by the action of methyl magnesium bromide on ethyl  $\beta$ -chloroisovalerate does not lose hydrogen chloride even when

treated with dilute alkali, it probably has the first of the above formulæ.

When isobutylene chlorohydrin,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Cl}$ , reacts with potassium cyanide the product consists of  $\beta$ -hydroxyisovaleronitrile  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CN}$ , a colourless, viscous liquid, b. p.  $130\text{--}132^\circ/30\text{ mm.}$ ,  $210\text{--}212^\circ/756\text{ mm.}$ , m. p.  $-12^\circ$ ,  $D^{20}_D 0.96762$ ,  $n_D 1.42911$ , with an unpleasant odour, which, unlike its  $\alpha$ -isomeride, can be distilled without decomposition. This nitrile reacts with acetyl chloride or acetic anhydride, forming the acetate,  $\text{OAc}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CN}$ , a mobile liquid, b. p.  $115\text{--}120^\circ/35\text{ mm.}$ ,  $198\text{--}200^\circ/758\text{ mm.}$ ,  $D^{18}_D 0.9951$ ,  $n_D 1.4193$ , and with phosphorus pentachloride, giving partly a chloro-derivative and partly the unsaturated nitrile,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CN}$ , identical with that obtained by the dehydration of  $\alpha$ -hydroxyisovaleronitrile.

The formation of an acetate differentiates the  $\beta$ -hydroxyisovaleronitrile from the analogous *tert.*-butanol, which gives, not an acetate, but a chloride, and shows that the cyanogen group influences the tertiary hydroxyl even when separated from it by a methylene group.  $\beta$ -Hydroxyisovaleronitrile reacts with methyl magnesium bromide, giving a mixture of mesityl oxide and diacetone alcohol; it is readily hydrolysed with potassium hydroxide, giving  $\beta$ -hydroxyisovaleric acid, but the ester of the latter can only be obtained pure by the action of ethyl iodide on the silver salt. Ethyl  $\beta$ -hydroxyisovalerate, when treated with Grignard's reagent, gives  $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol, but, owing to the difficulty in preparing the ester, its use was abandoned in favour of the following method.

Diacetone alcohol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$  (1 mol.), prepared as described by Heintz (*Annalen*, 1875, 178, 342), reacts with magnesium methyl bromide (2 mols.), giving  $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol,



a viscous liquid, b. p.  $113^\circ/35\text{ mm.}$ ,  $D^{20}_D 0.9206$ ,  $n_D 1.4375$ , already prepared by Franke (*Abstr.*, 1907, i, 171, 816). This diol when distilled at atmospheric pressure is partly dehydrated, giving  $\beta\delta$ -dimethyl- $\Delta^{\alpha}$ -pentene- $\delta$ -ol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CMe}:\text{CH}_2$ , a reaction entirely analogous to that undergone by the chlorohydrin, but differing from the dehydration of diacetone alcohol and  $\beta$ -hydroxyisovaleronitrile. The conclusion is drawn that the influence of a  $\text{C}(\text{OH})$  group is different from that of a carbonyl or cyano-group on an adjacent methylene group.  $\beta\delta$ -Dimethylpentane- $\beta\delta$ -diol is only very slightly oxidised to dihydroxytetramethylacetone by twenty-four hours' contact with dilute potassium permanganate solution.

Two series of reactions are suggested for the preparation of pentamethylglycerol, one starting from  $\gamma$ -chloro- $\beta$ -butanone, the other from  $\alpha$ -hydroxy- $\alpha$ -methylpropionitrile.

E. H.

**Preparation of Chlorohydrin from Glycerol and Sulphur Chloride.** DEUTSCHE SPRENGSTOFF AKTIEN-GESELLSCHAFT (D.R.-P. 201230).—Although dichlorohydrin is the product of the action of sulphur chloride on glycerol at  $100^\circ$ , it has now been found possible to obtain chiefly chlorohydrin by operating with the calculated amount of the chloride at  $25^\circ$  and then at  $50\text{--}70^\circ$ . In this way 85—95% of the glycerol is converted into the monochloro-derivative,

only about 1—2% of the dichloro-compound being produced. The chief product is purified by distillation under reduced pressure.

G. T. M.

**Halogen Ethers.** A. KARVONEN (*Ber.*, 1909, 42, 687—692).—According to Palomaa (*Diss. Helsingfors*, 1908) the reactivity of the halogen in haloid derivatives of aliphatic ethers varies with the position of the halogen atom with respect to oxygen. Preliminary experiments show that tripropylamine does not react with ethyl  $\beta$ -iodoethyl ether at 100°.

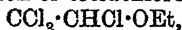
**Methyl  $\beta$ -iodoethyl ether**,  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$ , is obtained by the action of methyl alcohol on ethylene iodide at 100°, and may be obtained pure by distilling several times over solid sodium hydroxide. It has a sweet odour and b. p. 137.8°/750 mm., and  $D_4^{15}$  1.8322. It does not turn brown when exposed to diffused light for several months, and its aqueous or alcoholic solution yields a precipitate with silver nitrate.

**Ethyl  $\beta$ -iodoethyl ether** (Baumstark, *Ber.*, 1874, 7, 1172; Henry, *Abstr.*, 1885, 882; Demole, *Ber.*, 1876, 9, 743) is best purified by distillation over solid sodium hydroxide. It has b. p. 154.9—155.2°/761 mm. and  $D_4^{15}$  1.6698.

**$\beta$ -Iodoethyl propyl ether**,  $\text{CH}_2\text{Et}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$ , has b. p. 175—175.3°/750 mm. and  $D_4^{15}$  1.5379.

J. J. S.

**Preparation and Physical Properties of *as*-Tetrachloroethyl Ether.** FRED NEHER and WILLIAM FOSTER (*J. Amer. Chem. Soc.*, 1909, 31, 410—412).—A modification of Henry's method (*Abstr.*, 1871, 255) for the preparation of tetrachloroethyl ether,



is described, by means of which the compound can be obtained in a yield of 55—74% of the theoretical. *as*-Tetrachloroethyl ether boils at 189.4°/749.1 mm. (corr.) or 79°/16 mm., and has  $D_4^{15}$  1.4225.

E. G.

***as*-Dichlorovinyl Ethyl Ether: its Preparation from Tetrachloroethyl Ether and its Physical Properties.** FRED NEHER and WILLIAM FOSTER (*J. Amer. Chem. Soc.*, 1909, 31, 412—414).—*as*-Dichlorovinyl ethyl ether,  $\text{CCl}_2\cdot\text{CH}\cdot\text{OEt}$  (Godefroy, *Abstr.*, 1886, 607), can be obtained in a yield of 80—90% of the theoretical by the action of zinc on an alcoholic solution of *as*-tetrachloroethyl ether at a temperature below 40°. At higher temperatures the product contains a varying amount of dichloroacetal.

*as*-Dichlorovinyl ethyl ether boils at 144.2°/765.3 mm. (corr.), and has  $D_4^{15}$  1.2096 and  $D_4^{20}$  1.2081.

E. G.

**Difluoroethyl Bromide and Tetrafluorodiethyl Hydrogen Phosphate.** FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1909, 60—65).—When difluoroethyl alcohol (1 gram-molecule) is acted on by bromine (1 gram-atom) in the presence of excess of phosphorus, about 25% of the alcohol is recovered unchanged, another 25% is transformed into

difluoroethyl bromide, whilst the remainder is converted into a syrupy liquid, b. p. 253—255°, the analysis and vapour density of which prove it to be *difluoroethyl phosphate*,  $\text{PO}(\text{OC}_2\text{H}_3\text{F}_2)_3$ . The reaction producing this substance might be represented by either of the two equations: (1)  $\text{P} + 5\text{Br} + 4\text{C}_2\text{H}_3\text{F}_2 \cdot \text{OH} = (\text{C}_2\text{H}_3\text{F}_2)_3\text{PO}_4 + \text{C}_2\text{H}_3\text{F}_2\text{Br} + 4\text{HBr}$ ; (2)  $5\text{P} + 25\text{Br} + 20\text{C}_2\text{H}_3\text{F}_2 \cdot \text{OH} = 4(\text{C}_2\text{H}_3\text{F}_2)_{2/3}\text{PO}_4 + 8\text{C}_2\text{H}_3\text{F}_2\text{Br} + 17\text{HBr} + \text{H}_3\text{PO}_4$ . The amount of hydrogen bromide found experimentally is in favour of the former equation. The difluoroethyl bromide formed is identical with that obtained from tribromoethane (Abstr., 1908, i, 752).

Difluoroethyl phosphate is saponified by ammonia, giving *ammonium tetrafluorodiethyl phosphate*,  $\text{NH}_4\text{PO}_4(\text{C}_2\text{H}_3\text{F}_2)_2$ , which forms beautiful white, crystalline spangles, and is converted by baryta into the *barium* salt. The salts of silver and lead are both soluble in water, but the *mercurous* salt forms a white, crystalline precipitate insoluble in nitric acid. Tetrafluorodiethyl hydrogen phosphate is remarkably stable towards both acids and alkalis. Heating with excess of nitric acid on a water-bath for thirty-six hours is required in order to obtain the phosphate reaction with ammonium molybdate. E. H.

**New Method of Extracting a Phosphated Compound (Phytin) from Plants.** ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 64—67).—The author gives the following method for extracting from rice bran the phytin obtained from different sources by several investigators (compare Suzuki and Yoshimura, Abstr., 1908, ii, 124).

The finely-ground rice bran is treated with twice its weight of 0.2—0.3% hydrochloric acid, and the liquid separated by pressing, heated below its boiling point, and neutralised by means of recently-calced magnesium oxide. The precipitate formed, after washing several times with hot water by decantation, is dissolved in hydrochloric acid, and the solution filtered, decolorised with animal charcoal, and neutralised with magnesium oxide. After re-dissolving and again precipitating, the calcio-magnesium derivative of phytin is obtained. The composition of this compound corresponds with that of the calcio-magnesium derivative of the compound,  $\text{O}[\text{CH}_2 \cdot \text{O} \cdot \text{P}(\text{OH})_2]_3$ , described by Posternak (Abstr., 1903, ii, 607, 679, 680). The phytin separated in the above manner behaves like an ordinary ester, but is not so readily hydrolysed by alkalis as the latter. T. H. P.

**Effect of Neutral Salts on Hydrolysis by Water.** DAVID R. KELLOGG (*J. Amer. Chem. Soc.*, 1909, 31, 403—405).—It is well known that ester hydrolysis in the presence of a strong acid is greatly accelerated by the addition of a neutral salt of the acid. Experiments have now been carried out with the object of ascertaining the effect of neutral salts on the rate of hydrolysis in the absence of acids. Ethyl acetate was heated in sealed tubes with water, with potassium chloride solutions of 1%, 10%, and 20% strength, and with a saturated solution of this salt. The results show that the 1% solution produces a considerable acceleration, the 10% solution a much larger acceleration, whilst the 20% solution has but little effect, and a saturated solution exerts a strong inhibiting influence. E. G.

[Preparation of Salts of Iodated Fatty Acids.] FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 202353. Compare Abstr., 1908, i, 122, 123, 310).—*Manganous iodobehenate*, a white, amorphous mass, is obtained by adding an aqueous solution of manganous chloride to potassium iodobehenate in alcoholic solution. The corresponding *manganic*, *ferrous*, and *ferric* salts are prepared similarly. G. T. M.

[Iodination of the Higher Fatty Acids and Esters.] J. D. RIEDEL (D.R.-P. 202790).—Ethyl oleate dissolved in alcohol is treated with iodine and mercuric oxide, and, after twenty-four hours, freed from iodine with potassium iodide and thiosulphate. The final residue, after distilling off the solvent, contains 15–26% of iodine. G. T. M.

*Elæostearic Acid*. RIKO MAJIMA (*Ber.*, 1909, 42, 674–680).—The composition  $C_{18}H_{32}O_2$ , ascribed by Kametaka (*Trans.*, 1903, 83, 1042) to the solid acid, m. p. 48–49°, b. p. 235°/12 mm., in carbon dioxide isolated from oil of *Elæococca Vernicia*, and regarded by Cloez as elæomargaric acid,  $C_{17}H_{30}O_2$ , and by Maquenne as elæostearic acid,  $C_{18}H_{30}O_2$  (Abstr., 1903, i, 62), has been confirmed by the author, who has prepared a *dioxonide*,  $C_{18}H_{32}O_8$ , a yellow, amorphous, semi-solid substance. The products of its decomposition by water include valeraldehyde (thiosemicarbazone, m. p. 65°), valeric acid (anilide, m. p. 60°), azelaic acid, and its semialdehyde (semicarbazone, m. p. 165°). Consequently, elæostearic acid must have its double linkings between the fifth and the sixth and the ninth and the tenth carbon atoms. Succinaldehyde, succinic acid, and its semialdehyde cannot be detected, although the aqueous solution of the decomposition products contains a substance which responds to the pyrrole test. C. S.

*Preparation of Ethyl Glyoxylate by the Reduction of Ethyl Oxalate*. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 201895).—Ethyl oxalate, when reduced with sodium amalgam and absolute alcohol, yields ethyl glyoxalate, a 30–40% yield of which is obtained in the form of an alcoholate after precipitating the sodium as sodium oxalate and distilling the filtrate from this salt under reduced pressure. The ester itself is obtained by treating the alcoholate with phosphoric oxide. G. T. M.

*Syntheses by means of Mixed Organo-metallic Compounds of Zinc*. Preparation of Ketonic Acids and Diketones. EDMOND BLAISE and A. KÖHLER (*Compt. rend.*, 1909, 148, 489–491. Compare Abstr., 1907, i, 749; 1908, i, 248).—The acid esters of the succinic and glutaric series of dibasic acids are readily prepared by the action of acetic anhydride on the acid anhydride. In the case of the higher homologues, it is necessary to mix the normal ester with an alcoholic solution of sodium ethoxide and add the calculated amount of water. Conversion of the acid esters into the corresponding chlorides is best effected by means of thionyl chloride. The following ketonic acids have been prepared by the action of mixed organo-metallic zinc compounds on the chlorides so obtained: *ε-keto-octioic acid*,  $COMe \cdot [CH_2]_5 \cdot CO_2H$ , m. p. 31–32°; *ε-ketononoic acid*,  $C_9H_{16}O_3$ , m. p.

52°;  $\eta$ -ketodecic acid,  $C_{10}H_{18}O_3$ , m. p. 42°;  $\theta$ -ketoundecic acid,  $C_{11}H_{20}O_3$ , m. p. 64°;  $\delta$ -keto-octic acid,  $C_8H_{14}O_3$ , m. p. 53°.

The corresponding symmetrical diketones are obtained in good yield when the dichlorides of the dibasic acids are treated with the organo-metallic zinc compounds. The reaction, however, is not available in the succinic and glutaric series, since in this instance lactones are obtained. The following diketones are mentioned: *undecane- $\gamma$ -dione*,  $COEt \cdot [CH_2]_5 \cdot COEt$ , m. p. 68°; *decane- $\beta$ -dione*,  $C_{10}H_{18}O_2$ , m. p. 64°; *dodecane- $\gamma$ -dione*,  $C_{12}H_{22}O_2$ , m. p. 72°; *undecane- $\beta$ -dione*.

W. O. W.

**Halogen Derivatives of  $\gamma$ -Hydroxycrotonic Acid.** ROBERT LESPIEAU and VIGUIER (*Compt. rend.*, 1909, 148, 419—422. Compare *Abstr.*, 1908, i, 125).—The authors describe further experiments with  $\alpha\beta$ -dibromo- $\gamma$ -hydroxy- $\Delta^2$ -butenoic acid which favour the view that this compound belongs to the maleic rather than to the fumaric series. The acid differs from Tönnies' lactone in yielding a *potassium* salt,  $OH \cdot CH_2 \cdot CBr \cdot CBr \cdot CO_2K, H_2O$ . It appears, therefore, that this lactone, to which Hill ascribed the constitution  $\begin{array}{c} CBr-CO \\ | \quad \diagup \\ CBr-CH_2 \end{array} > O$  (*Abstr.*, 1894, i, 319), is not a simple derivative of the acid. The acid, however, undergoes conversion into the lactone when its aqueous solution is saturated with hydrogen chloride.

Hydrogen bromide converts  $\gamma$ -hydroxytetrollic acid into a mixture of  *$\alpha$ -bromo- $\gamma$ -hydroxy- $\Delta^2$ -butenoic acid*,  $OH \cdot CH_2 \cdot CH \cdot CBr \cdot CO_2H$ , m. p. 158—160°, and Hill's lactone,  $\begin{array}{c} CH-CO \\ | \quad \diagup \\ CBr-CH_2 \end{array} > O$  (*loc. cit.*). Bromine converts the latter into Hill's dibromolactone. The bromo-acid probably belongs to the fumaric series.

Iodine and potassium iodide convert  $\gamma$ -hydroxytetrollic acid into  *$\alpha$ - $\beta$ -di-iodo- $\gamma$ -hydroxy- $\Delta^2$ -butenoic acid*,  $OH \cdot CH_2 \cdot CI \cdot CI \cdot CO_2H$ , m. p. 173—175° (decomp.). Hydrogen bromide converts this into a lactone, m. p. 143—145°, which has not yet been obtained pure.

W. O. W.

**Action of Oxalic Acid on Ferric Hydroxide.** FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1909, 13, 157—158).—The solubility of ferric hydroxide in solutions of oxalic acid of varying strengths has been determined at 25°. The results show that the solubility of the hydroxide is directly proportional to the concentration of the acid, and that no definite basic ferric oxalate is formed from solution at 25°. In all solutions more iron is present than is equivalent to the oxalic acid present, but the solutions have an acid reaction.

G. S.

**Conversion of Active  $\alpha$ -Bromopropionic Acid into Active Methylsuccinic Acid.** EMIL FISCHER and ERICH FLATAU (*Annalen*, 1909, 365, 13—20).—The authors have attempted to increase the number of direct syntheses of optically active substances by replacement of some atom or group attached to the asymmetric carbon atom of an active compound. For this purpose the synthesis of an active

methylsuccinic acid from ethyl sodiocyanoacetate and ethyl *l*-α-bromopropionate was selected, and Bone and Sprankling's method (Trans., 1899, 75, 839) was used.

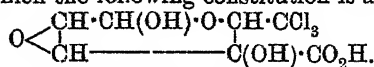
In the condensation care was taken to keep the temperature as low as possible (below 35°) in order to avoid racemisation. The ethyl cyanomethylsuccinate had b. p. 119–153°/10 mm. and α – 17·6° in a 100 mm. tube. It was hydrolysed to propane-ααβ-tricarboxylic acid by shaking with fuming hydrochloric acid at the ordinary temperature, and the acid isolated as the insoluble barium salt. The acid was crystallised from a mixture of ether and benzene; it had m. p. 150° (decomp.) and  $[\alpha]_D^{20}$  – 33·8° in aqueous, or – 57·8° in sodium hydroxide, solution. The acid was decomposed by heating the aqueous solution at 100° for four hours, a levorotatory methylsuccinic acid was obtained, but the rotation varied considerably with different specimens, and was always below the value obtained by Ladenburg (Abstr., 1895, i, 449).

The possibility of the Walden inversion occurring during the synthesis is mentioned. J. J. S.

#### Chemical Treatment of Bile. Separation of the Bile Acids.

MAURICE PIETTRE (*Compt. rend.*, 1909, 148, 372–374).—After extraction with ether, the bile is desiccated, powdered, and extracted with boiling methyl alcohol. After filtration, the boiling solution is precipitated drop by drop with barium methoxide (compare Étard and Vila, this vol., i, 124), which carries down the pigments. As soon as the solution becomes alkaline, the precipitation is stopped, and the excess of barium is removed by carbon dioxide; the bile salts can now be readily obtained from the clear, colourless solution. The barium methoxide precipitate, after acidification and washing, is extracted with chloroform and yields bilirubin. G. B.

**Chloralic Acids.** MAURICE HANRIOT (*Compt. rend.*, 1909, 148, 487–489. Compare Abstr., 1893, i, 247; 1894, i, 105; 1895, i, 321; 1896, i, 519).—The compounds of chloral with certain sugars, which the author has termed chloraloses, undergo oxidation when treated with potassium permanganate and sulphuric acid or with nitric acid, giving acids to which the following constitution is ascribed:



In the case of mannochloralose a lactone was obtained on oxidation. α-Glucochloralic acid, C<sub>7</sub>H<sub>7</sub>O<sub>6</sub>Cl<sub>3</sub>, forms slender needles, m. p. 212°. β-Glucochloralic acid, C<sub>7</sub>H<sub>7</sub>O<sub>6</sub>Cl<sub>3</sub>·2H<sub>2</sub>O, occurs as efflorescent, rhombic tablets, and forms a sparingly soluble sodium salt. The lactone, C<sub>7</sub>H<sub>5</sub>O<sub>5</sub>Cl<sub>3</sub>, obtained by the action of acetyl chloride or zinc chloride on the acid, has m. p. 185°. β-Galactochloralic acid, C<sub>7</sub>H<sub>7</sub>O<sub>6</sub>Cl<sub>3</sub>, m. p. 307°, forms a lactone, C<sub>7</sub>H<sub>5</sub>O<sub>5</sub>Cl<sub>3</sub>, m. p. 130°. Manno-chloralic lactone, C<sub>8</sub>H<sub>7</sub>O<sub>6</sub>Cl<sub>3</sub>, is sparingly soluble in water, and has m. p. 242°; it dissolves in aqueous ammonia, forming the ammonium salt of the unstable acid. α-Arabinochloralic acid, C<sub>7</sub>H<sub>7</sub>O<sub>6</sub>Cl<sub>3</sub>, forms needles, m. p. 320°; the β-acid is identical with β-galactochloralic acid.

$\beta$ -Xylochloralic acid is identical with  $\beta$ -glucochloralic acid.

W. O. W.

**Action of Nitric Anhydride on Mucic Acid.** A. CRUM BROWN and G. E. GIBSON (*Proc. Roy. Soc. Edin.*, 1908, 23, 96—97).—Mucic acid and nitric anhydride, both previously cooled in ice, were mixed together and left in a vacuum over sodium hydroxide; on extracting with ether in a Soxhlet tube, and evaporating at the ordinary temperature with a vacuum pump, colourless needles were obtained, which on exposure to air or in a vacuum soon changed to a white powder. The analyses of this substance, although discordant, correspond with a tetranitrate. In the air, the white solid soon begins to decompose with evolution of nitric acid and oxides of nitrogen; on heating, it decomposes violently.

P. H.

**The Reduction Products of Sulphurous Acid and their Double Compounds with Aldehydes.** CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 202825, 202826, and 202827).—The double sodium salt,  $\text{HO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}, \text{HO}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{ONa}$ , is produced by passing sulphur dioxide into a mixture of zinc dust and aqueous formaldehyde until the metal has dissolved, and then treating the solution with sodium carbonate. A sparingly soluble benzaldehyde zinc hyposulphite can be similarly obtained.

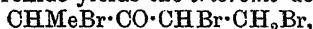
When half the proportions of aldehyde and sulphurous acid are employed, salts of the type  $\text{HO}\cdot\text{CHR}\cdot\text{O}\cdot\text{SO}\cdot\text{Zn}\cdot\text{OH}$  are formed; these have twice as much reducing action on indigotin as the foregoing double salts.

Sodium formaldehyde sulphonylate,  $\text{HO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SONa}$ , is obtained in stable, well defined crystals by evaporating its solutions under greatly reduced pressure and separating the product from the liquid without allowing it to cool.

G. T. M.

**Bromo-ketones.** J. PASTUREAU (*Bull. Soc. chim.*, 1909, [iv], 5, 226—227. Compare Abstr., 1905, i, 572; 1907, i, 113, 185).—A description of bromo-derivatives of homologues of acetone obtained as already described (*loc. cit.*) from the ketone peroxides.

Diethyl ketone peroxide yields the tribromo-derivative,



b. p.  $142^\circ/100\text{ mm.}$ , D 2.003, which on hydrolysis with potassium carbonate gives the *keto-alcohol*,  $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ . The latter reduces strongly in the cold, and gives a *phenylosazone*, m. p.  $180\text{—}181^\circ$ .

Methyl propyl ketone peroxide, under the same conditions, yields the tetrabromo-derivative,  $\text{CHMeBr}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CBr}_3$ , m. p.  $57^\circ$ , which separates from boiling alcohol in colourless rhombohedra and hexagonal prisms. On hydrolysis with potassium carbonate, it yields the lactone,  $\text{CO}\text{—}\text{CO}$   
 $\text{CH}_2\cdot\text{CHMe}\text{>O}$ , of which the corresponding hydroxy-acid has only been obtained in the form of the lead salt by hydrolysing the tetrabromo-derivative with litharge in a closed vessel.

T. A. H.

**Oxidation of Ketones and Diketones by Hydrogen Peroxide in Presence of Acid.** J. PASTUREAU (*Bull. Soc. chim.*, 1909, [iv], 5, 227—229. Compare Baeyer and Villiger, *Abstr.*, 1900, i, 133; Pastureau, *Abstr.*, 1905, i, 572, and 1907, i, 113, 185).—The author has shown already that aliphatic ketones yield, on treatment with hydrogen peroxide in presence of dilute sulphuric acid, the corresponding ketone peroxides and hydroxy-ketones, acetone furnishing acetone peroxide and acetol (acetyl-carbinol). In the present paper this reaction is applied to other products of this class.

Diethyl ketone peroxide, D 1·038, is a liquid insoluble in water (compare Baeyer and Villiger, *loc. cit.*), and with it is formed *propionylmethylcarbinol*,  $\text{COEt} \cdot \text{CHMe} \cdot \text{OH}$ , which with phenylhydrazine yields acetylpropionyl phenylosazone, m. p. 136°.

Methyl propyl ketone peroxide, D 1·006, is formed along with the keto-alcohol,  $\text{CH}_3\text{Ac} \cdot \text{CHMe} \cdot \text{OH}$ . Acetophenone yields only hydroxy-acetophenone,  $\text{OH} \cdot \text{CH}_2 \cdot \text{COPh}$ , and benzoic acid.

The diketones, which contain a carbonyl group between two open-chain radicles, yield peroxides, but not those in which the two carbonyl groups are contiguous with closed-chain radicles. These peroxides are highly polymerised, vitreous solids, which are not volatile in steam, but have properties akin to those of the peroxides of the simple ketones (*loc. cit.*). *Acetylacetone peroxide*,  $(\text{C}_5\text{H}_{10}\text{O}_4)_n$ , is formed along with a *keto-alcohol*, which condenses with phenylhydrazine to form a pyrazole and gives a red coloration with ferric chloride. *Benzoylacetone peroxide*,  $(\text{C}_{10}\text{H}_{10}\text{O}_3)_n$ , is obtained together with benzoic acid. Dibenzoylmethane and benzil furnish each 2 mols. of benzoic acid, whilst benzoin is decomposed, yielding a little benzoic acid.

T. A. H.

**Preparation of Diacetyldioxime [Dimethylglyoxime].** HEINRICH BILTZ (*Zeitsch. anal. Chem.*, 1909, 48, 164—165. Compare Tschugaeff, *Abstr.*, 1905, ii, 613).—Fifty grams of methyl ethyl ketone are dissolved in 100 grams of ether, the solution is cooled in ice, and eighty-two grams of amyl nitrite are added drop by drop while a current of hydrogen chloride is being passed. After a few hours, 150 c.c. of iced water and 50 c.c. of 33% aqueous sodium hydroxide are added, and, after thorough shaking, the alkaline solution is drawn off and the ether is shaken a few times with dilute sodium hydroxide solution. The alkaline solutions are united and shaken with a little ether, and then evaporated on the water-bath to remove the dissolved ether. When cold, the solution is carefully neutralised with dilute sulphuric acid, and a solution of 50 grams of hydroxylamine hydrochloride in 75 c.c. of water is added. After remaining overnight, the crystalline mass is collected, using suction, and then purified by recrystallisation; the yield amounts to 45—50 grams.

L. DE K.

**Simple Notation for Indicating the Configuration of the Sugars and Allied Substances.** THOMAS S. PATTERSON (*Chem. News*, 1909, 99, 124—126).—The empirical names of the compounds are retained. Attention is confined to the  $-\text{OH}$  groups on the right-

hand side of the formula, in which the most highly oxidised end of the chain is always placed uppermost, and the asymmetric carbon atoms are numbered from *below upwards*.

Thus, on the right-hand side of the formula for *d*-arabinose, hydroxyl groups are found on the first and second carbon atoms, and the symbol *d*-arabinose (1:2) is applied. Similarly, we have *d*-glucose (1:2:4) and *l*-ribose (0), there being no hydroxyl group on the right-hand side. For substances having the same group at either end of the molecule, two different symbols are possible; thus *d*-sorbitol is written  $\begin{smallmatrix} (1:2:4) \\ (3) \end{smallmatrix}$ . In *d*-idosaccharic acid (2:4) the two symbols are identical. For inactive substances, for example, dulcitol  $\begin{smallmatrix} (1:4) \\ (2:3) \end{smallmatrix}$ , the second symbol is entirely different from the first. E. F. A.

**Behaviour of Cellobiose and its Osone towards Certain Enzymes.** EMIL FISCHER and GÉZA ZEMPLÉN (*Annalen*, 1909, 365, 1—6).—The disaccharide cellobiose (Skraup and König, Abstr., 1901, i, 370; 1902, i, 135) is readily hydrolysed by emulsin, but is not affected by the extract of dry *Frohberg* yeast or yet by the enzymes of *Aspergillus niger* or kephir lactase.

Cellobiososone, obtained from the osazone, is a syrup which sets to a viscous mass, and in its behaviour towards enzymes resembles cellobiose. The behaviour of the disaccharide is similar to that of gentiobiose (Abstr., 1902, i, 744), isomaltose (Abstr., 1896, i, 119), and to a certain extent milk sugar. In all these compounds it is probable that the two molecules of dextrose are united in the same manner, and that in maltose the condensation is of a different type. J. J. S.

**Colloidal Properties of Starch in Relation to its Chemical Constitution.** EUGÈNE FOUARD (*Compt. rend.*, 1909, 148, 502—505. Compare this vol., i, 13).—When potassium hydroxide is added in increasing quantities to a perfectly clear starch solution (filtered through collodion), the rotatory power of the latter diminishes, at first rapidly, then more slowly, and finally it approaches asymptotically to the rotatory power for a maltose solution. The change is reversible, so that the rotation increases again on neutralisation; there is a definite rotation for every degree of alkalinity. The rotatory power of the part remaining dissolved when a starch solution gradually gelatinises diminishes while gelatinisation proceeds, and the final portions to be gelatinised have a rotation also approaching asymptotically to that of pure maltose. Starch is therefore to be regarded as being simply a condensation product of maltose of varying degrees of complexity. G. B.

**Course of the Oxidation and Hydrolysis of Starch and its Constituents by Hydrogen Peroxide.** Z. GATIN GRUZEWSKA (*Compt. rend.*, 1909, 148, 578—580).—Hydrogen peroxide hydrolyses starch and at the same time oxidises it, the final products being maltose and oxalic acid. The constituents of starch, amylopectin, and amylose are acted on in different ways by hydrogen peroxide (as they

are by diastase). In the case of both constituents, dextrans are formed as intermediate products. In the case of amylopectin the attack on the micellæ appears to be simultaneous, in that of amylose successive.

G. B.

**Cellulose Hydrates.** HERMANN OST and F. WESTHOFF (*Chem. Zeit.*, 1909, 33, 197. Compare Abstr., 1907, i, 390).—The name cellulose hydrate has been used by Cross and Bevan (*Trans.*, 1895, 67, 433) to designate substances which contain besides hygroscopic water, also water more firmly retained, such as is present in mercerised cellulose, the composition of which is given as  $2C_6H_{10}O_5 \cdot H_2O$ . The hydrocelluloses are substances which, in the dry state, contain water in chemical combination; they have the composition  $(C_6H_{10}O_5)_n \cdot H_2O$ , and it has been shown by Schwalbe (*Abstr.*, 1907, i, 390) that cellulose hydrate is quite different from hydrocellulose.

The present paper records a careful comparison of dried cellulose, cellulose hydrate, and hydrocellulose, and, from the results of the estimation of water driven off at 110–130° and from analyses, the conclusion is drawn that mercerised cellulose contains more hygroscopic water than hydrocellulose; further, that the so-called cellulose hydrates (mercerised cellulose, etc.), when freed from water by drying at 120–125°, have the same composition as ordinary cellulose, namely,  $(C_6H_{10}O_5)_n$ .

Hydrocellulose, on the other hand, when in the anhydrous state has the composition represented by the formulæ  $C_{60}H_{102}O_{51}$ ,  $C_{36}H_{52}O_{31}$ , etc., analogous to the hydrolytic decomposition products of starch.

J. V. E.

**Putrefaction of Glutamic and Aspartic Acids.** L. BORCHARDT (*Zeitsch. Physiol. Chem.*, 1909, 59, 96–100).—During putrefaction, glutamic acid yields butyric acid as a result of de-amidation and evolution of carbon dioxide. Aspartic acid also loses  $NH_2$ , and is converted into succinic acid, and finally, by loss of carbon dioxide, into propionic acid. Volatile bases other than ammonia were not detected.

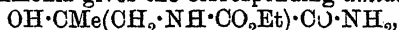
W. D. H.

**Preparation of Alkyl Dialkylamino- $\alpha$ -trichloro- $\beta$ -hydroxyethoxyisobutyrate.** LES ETABLISSEMENTS POULENC FRÈRES and ERNST FOURNEAU (D.R.-P. 203643).—Esters having pronounced saporific properties with low toxicity are produced by condensing anhydrous chloral with the alkyl dimethylaminohydroxyisobutyrate. *Ethyl dimethylamino- $\alpha$ -trichloro- $\beta$ -hydroxyethoxyisobutyrate*,

$CCl_3 \cdot CH(OH) \cdot O \cdot CMe(CH_2 \cdot NMe_2) \cdot CO_2Et$ , rectangular prisms, m. p. 66–67°, b. p. 140–142°/22 mm., *hydrochloride*, needles, m. p. 181–182°, and *propyl dimethylamino- $\alpha$ -trichloro- $\beta$ -hydroxyethoxyisobutyrate*, transparent crystals, m. p. 65°, were thus obtained. These esters, when exposed to moist air, undergo hydrolysis to the acid,  $CCl_3 \cdot CH(OH) \cdot O \cdot CMe(CH_2 \cdot NMe_2) \cdot CO_2H$ . G. T. M.

**Aminohydroxy-acids. II. Amino-derivatives of  $\alpha$ -Hydroxyisobutyric Acid.** ERNEST FOURNEAU (*Bull. Soc. chim.*, 1909, [iv], 5, 229–241. Compare Abstr., 1907, i, 622).—Much of the work now

recorded has been published previously (Abstr., 1908, i, 937), and in this paper fuller experimental details are given and a number of additional derivatives described. The starting point of the investigation was  $\beta$ -chloro- $\alpha$ -hydroxyisobutyronitrile, b. p. 103—104°/16 mm., which was converted into the corresponding acid, of which the *ethyl* ester, b. p. 197°/765 mm. or 106°/30 mm., *propyl* ester, b. p. 217°/765 mm. or 106—107°/16 mm., and *amyl* ester, b. p. 241—242°/765 mm. or 115—116°/12 mm., were prepared. The acid on treatment with ammonia solution in a closed vessel yields  $\beta$ -amino- $\alpha$ -hydroxyisobutyric acid, which is crystalline, decomposes at 281°, and yields a crystalline *hydrochloride* and *sulphate*. The *ethyl* ester (*loc. cit.*) furnishes an *isovaleryl* derivative, b. p. 194—196°/21 mm., a *urethane*,  $\text{OH}\cdot\text{CMe}(\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et})\cdot\text{CO}_2\text{Et}$ , b. p. 164—165°/16 mm. (which with alcoholic ammonia gives the corresponding *amide*,



m. p. 125°, silky needles), and a *propylurethane* derivative, b. p. 184°/30 mm. The *ethyl* ester condenses with potassium isocyanate, and on treating the product with hydrochloric acid, 5-*hydroxy-5-methyl-dihydroureacil*,  $\text{NH}\langle\begin{smallmatrix} \text{CO}\cdot\text{CMe}(\text{OH}) \\ \text{CO}\text{---}\text{NH} \end{smallmatrix}\rangle\text{CH}_2$ , crystallising in colourless tablets from boiling water, is obtained.

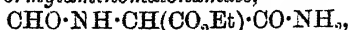
The *propyl* and *amyl* esters of  $\beta$ -amino- $\alpha$ -hydroxyisobutyric acid were also prepared; their *urethanes* are colourless, syrupy liquids, which are soluble in water, and have b. p. 167—168°/14 mm. and 173—174°/12 mm. respectively.

In preparing *ethyl*  $\beta$ -methylamino- $\alpha$ -hydroxyisobutyrate (*loc. cit.*) by esterifying the acid in the usual manner, some *ethyl methylaminobis-hydroxyisobutyrate*,  $\text{NMe}[\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CO}_2\text{Et}]_2$ , b. p. 180°/17 mm., is obtained as a thick, oily liquid soluble in water. The *methylamide* of  $\beta$ -methylamino- $\alpha$ -hydroxyisobutyric acid, b. p. 157°/31 mm., is obtained by the action of methylamine on the original *ethyl chlorohydroxyisobutyrate* in presence of alcohol or benzene.

$\beta$ -*Dimethylamino- $\alpha$ -hydroxyisobutyric acid*, m. p. 174°, crystallises in bulky, transparent tablets, and possesses a sweetish, slightly nauseous taste; the *benzoyl* derivative, m. p. 182°, crystallises in spangles, and the *amide*, m. p. 102°, in needles. The *ethyl* ester (*loc. cit.*) yields the following acyl derivatives: *valeryl*, b. p. 143—145°/20 mm., liquid; *bromovaleryl hydrochloride*, m. p. 142°, colourless prisms; *bromohexoyl hydrochloride*, m. p. 134°, quadrangular tablets; *p-nitrobenzoyl hydrochloride*, m. p. 196°, yellow prisms. The *propyl* ester (*loc. cit.*) furnishes a *valeryl* derivative, b. p. 148—150°/16 mm., a liquid having a feeble odour of smoked fish; its *hydrobromide*, m. p. 120°, is crystalline, possesses a burning taste, and is employed in medicine under the name "quietol." T. A. H.

**Derivatives of Oximinocyanoacetic Acid.** MAX CONRAD and ARNOLD SCHULZE (*Ber.*, 1909, 42, 735—742).—*Ethyl oximinocyanoacetate* is readily obtained in 87% yield by treating a cold mixture of *ethyl cyanoacetate* and aqueous sodium nitrite with glacial acetic acid and decomposing the resulting yellow, crystalline sodium derivative

with hydrochloric acid. It is changed by zinc dust and formic acid, D 1-22, into *ethyl formylaminomalonamate*,

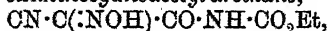


m. p. 142°, the constitution of which is proved by its conversion by concentrated ammonium hydroxide into formylaminomalonamide (this vol., i, 213). Ethyl oximinocynoacetate is readily oxidised by potassium permanganate to ethyl nitrocynoacetate, of which the *silver* and the *potassium* derivatives are described. Oximinocynoacetamide (deoxyfulminuric acid) is readily obtained by treating an aqueous solution of cyanoacetamide and sodium nitrite at 0° with glacial acetic acid and decomposing the resulting sodium derivative with the calculated quantity of hydrochloric acid; by reduction by zinc and formic acid it yields formylaminomalonamide, whilst oxidation by potassium permanganate leads to the formation of nitrocynoacetamide (fulminuric acid), the potassium salt of which is also obtained by the action of concentrated ammonium hydroxide on the potassium derivative of ethyl nitrocynoacetate.

Cyanoacetylcarbamide, obtained by heating carbamide, cyanoacetic acid, and acetic anhydride at 60° for three hours, reacts with sodium nitrite in hot water to form yellow crystals of the *sodium* derivative of oximinocynoacetylcarbamide,  $\text{C}_4\text{H}_3\text{O}_3\text{N}_4\text{Na}\cdot\text{H}_2\text{O}$ , which develops an intense violet coloration with ferrous sulphate and sodium hydroxide.

*Oximinocynoacetylcarbamide*,  $\text{CN}\cdot\text{C}(\text{:NOH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 220° (decomp.), is oxidised by potassium permanganate to the *potassium* derivative of nitrocynoacetylcarbamide.

*Cyanoacetylurethane*,  $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , m. p. 167—168°, prepared from urethane, cyanoacetic acid, and acetic anhydride, yields in a similar manner *oximinocynoacetylurethane*,



m. p. 201° (decomp.), which also gives a violet coloration with ferrous sulphate and sodium hydroxide. C. S.

**Action of Hydrazine on Ethyl Mesoxalate.** RICHARD S. CURTISS, ALFRED R. KOCH, and E. J. BARTELLS (*J. Amer. Chem. Soc.*, 1909, 31, 416—421).—In earlier papers (Curtiss, *Abstr.*, 1906, i, 339; Curtiss and Tarnowski, *Abstr.*, 1908, i, 760) the action of ammonia and hydrazine on esters of mesoxalic acid has been described.

When ethyl dihydroxymalonate is treated with an aqueous solution of hydrazine hydrate or carbonate, *ethyl hydrazinobistartronate*,



m. p. 58°, is produced, which forms colourless, rhombohedral crystals, and has a bitter taste. It is stable in the air, but if left in a desiccator or carefully heated, water is eliminated and an oily substance is formed. The compound reduces silver nitrate and platonic chloride to the metallic state, and is decomposed by nitrous acid with production of nitrogen, ethyl dihydroxymalonate, and small quantities of a compound, m. p. 253°. Phosphorus pentachloride reacts with ethyl hydrazinobistartronate with evolution of hydrogen chloride, thus proving the presence of hydroxyl groups. When the compound is warmed with mercuric oxide, nitrogen and ethyl dihydroxymalonate are produced.

By the action of benzaldehyde on the hydrazine compound, benzalazine is formed, and by the action of benzoyl chloride or benzoic anhydride, a *dibenzoylhydrazine*, m. p. 241° (corr.), is produced.

When hydrazine hydrate solution is added to an alcoholic solution of ethyl mesoxalate, a *compound*,  $C_4H_{15}O_9N_2$ , m. p. 125—130° (decomp.), is obtained which crystallises in colourless needles. E. G.

**Reduction of the Esters of *d*-Alanine and of *dl*-Phenylalanine.** EMIL FISCHER and TOKUHEI KAMETAKA (*Annalen*, 1909, 365, 7—12. Compare Fischer, *Abstr.*, 1908, i, 323; Neuberg, *ibid.*, 322).—A 17% yield of *d*- $\alpha$ -aminopropionacetal,  $NH_2 \cdot CHMe \cdot CH(OEt)_2$ , is obtained when the *d*-alanine ethyl ester is reduced with sodium amalgam in slightly acid solution and the resulting amino-aldehyde treated with an alcoholic solution of hydrogen chloride at 0°. It is a colourless liquid, b. p. 55—56°/11 mm., has  $D^{20}_D$  0.902, and  $n_D$  1.41955. The solution in hydrochloric acid has  $[\alpha]^{19}_D + 14.5^\circ$ . The *picrate*,  $C_{13}H_{20}O_9N_4$ , crystallises from benzene in yellow prisms, m. p. 86° (corr.) after sintering at 82°. The *normal oxalate*,  $C_{16}H_{26}O_8N_2$ , separates as colourless plates when ethereal solutions of the components are mixed; it has m. p. 176° (corr., decomp.). The acetal can be readily hydrolysed, but the hydrochloride of the amino-aldehyde has not been obtained in a crystalline form.

*dl*- $\alpha$ -Amino- $\beta$ -phenylpropionacetal,  $CH_2Ph \cdot CH(NH_2) \cdot CH(OEt)_2$ , has b. p. 103—105° (corr.)/0.25 mm. or 153.5°/11 mm.,  $D^{20}_D$  0.995,  $n_D$  1.49383. It is practically insoluble in water, and does not reduce Fehling's solution. The *picrate*,  $C_{19}H_{24}O_9N_4$ , crystallises from benzene in small, yellow prisms or plates, m. p. 106—107° (corr.). J. J. S.

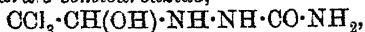
**Malonamide Derivatives.** MAX CONRAD and ARNOLD SCHULZE (*Ber.*, 1909, 42, 729—735).—Only one of the methylene hydrogen atoms of malonamide can be replaced by an alkyl group by treatment with sodium alkyl oxide and an alkyl halide. Methylmalonamide,  $CHMe(CO \cdot NH_2)_2$ , has m. p. 212°, and *ethylmalonamide*, m. p. 212—214°. *o*-Nitrobenzylmalonamide,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH(CO \cdot NH_2)_2$ , m. p. 234° (decomp.), is obtained from malonamide, sodium ethoxide, and a cold alcoholic solution of *o*-nitrobenzyl chloride.

The interaction of oximinomalonamide, formic acid, D 1.22, and zinc dust on the water-bath leads to the formation of *formylaminomalonamide*,  $HCO \cdot NH \cdot CH(CO \cdot NH_2)_2$ , m. p. 206° (decomp.), darkening at 195—200°. *Methyl formylaminomalonate*,  $CHO \cdot NH \cdot CH(CO_2Me)_2$ , m. p. 85°, b. p. 250° (decomp.), prepared in a similar manner from methyl oximinomalonate, is converted into the preceding compound by an excess of concentrated ammonium hydroxide. *Ethyl formylaminomalonate* has m. p. 48°. The reduction of oximinomalonic esters by zinc dust and 80% acetic acid yields glycine.

*Malonyldiurethane*,  $CH_2(CO \cdot NH \cdot CO_2Et)_2$ , obtained by heating malonic acid, urethane, and acetic anhydride for five hours on the water-bath, has m. p. 124°, yields ammonium barbiturate, urethane, and malonamide by treatment with ammonia, and by heating with a solution of sodium nitrite and decomposing the cold product with the calculated amount of hydrochloric acid, forms *nitrosomalonyldiurethane*,  $C_9H_{13}O_7N_3$ .

m. p. 203—204°, which gives a colourless solution with sodium hydroxide, a yellow solution with ammonium hydroxide, and in aqueous solution yields a deep blue precipitate by careful treatment with sodium hydroxide and ferrous sulphate. C. S.

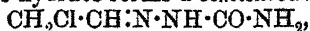
**Action of Semicarbazide on Chloroaldehydes.** ANDRÉ KLING (*Compt. rend.*, 1909, 148, 568—570).—Chloral hydrate or chloral alcoholate reacts readily with semicarbazide in aqueous solution, forming *chloral hydrate semicarbazide*,



an unstable, crystalline substance decomposing at 90°. When boiled with water or alcohol, it loses hydrogen chloride and forms the semicarbazone of glyoxylic acid.

When an alcoholic solution of dichloroacetaldehyde and semicarbazide is allowed to evaporate in a vacuum, *dichloroacetaldehyde semicarbazide*,  $\text{C}_2\text{H}_5\text{OCl}_2\text{N}_3$ , remains as a crystalline mass, m. p. 155—156° (decomp.). On boiling with water it is transformed into glyoxalsemicarbazone.

Chloroacetaldehyde hydrate forms a *semicarbazone*,



m. p. 134—135° (decomp.).

W. O. W.

**Desmotropy and Merotropy. VI. Constitution of Cyanic Acid.** ARTHUR MICHAEL and HAROLD HIBBERT (*Annalen*, 1909, 364, 129—146. Compare this vol., i, 91).—The authors have endeavoured to determine the constitution of cyanic acid by investigating the action of tertiary amines on the substance in the state of vapour and also in solution. The problem is complex on account of the ease of conversion into cyamelide, and the fact that, not only do the primary and secondary amines react in solution to give the corresponding salts, but also the tertiary amines, trimethylamine, triethylamine, and tripropylamine. The salt is mixed, in many cases, with cyamelide, the amount of the latter varying with the nature of the solvent. Triisoamylamine, however, does not give rise to salt formation in any solvent, the precipitate consisting exclusively of cyamelide; the same result is obtained by passing the vapour into the amine at  $-10^\circ$ . Since it is possible to prepare the salt indirectly, and it proves to be stable under the conditions just mentioned, the conclusion is drawn that cyanic acid in the state of vapour and in solution is really carbonimide,  $\text{CO} \cdot \text{NH}$ . The main support of the latter argument lies in the fact that triisoamylamine combines with the weakest acidic substances, such as phenols, to give stable salts, and its power of enolisation is practically non-existent. The salt formation in the case of the other tertiary amines is explained as follows: When a molecule of an amine,  $\text{NR}_3$ , comes into the sphere of action of a molecule of carbonimide,  $\text{O} \cdot \text{C} \cdot \text{NH}$ , there is in every case a tendency towards salt formation. This expresses itself in a primary attraction of the positive nitrogen of the amine for the negative oxygen of the carbonimide, in consequence of which the positive character of the former undergoes a considerable alteration. As

a result, it has a greater affinity for a positive element, for example, hydrogen, which, if pronounced enough, results in the migration to  $\text{OC:NH}$  it of the hydrogen of the carbonimide, as indicated thus :



If the character of the nitrogen of the amine is rendered strongly positive through the introduction of certain radicles, for example, *isoamyl*, then, in spite of the influencing of the negative oxygen atom, it has not the necessary affinity for hydrogen to enable it to separate the latter from the nitrogen of the carbonimide. *Triisoamylamine*, for this reason, does not yield a salt, but the large amount of free chemical energy in the molecule makes itself felt in the conversion of the carbonimide into cyamelide. From this point of view, salt formation does not presuppose the primary change  $\text{HNCO} \rightarrow \text{NCOH}$ , but represents the phenomenon of merotropisation, that is, the formation of a salt directly from a merotropic substance.

The influence of various solvents on the transformation of cyanates into the corresponding carbamides has also been investigated. It is found that there is no simple relation between the specific inductive capacity of the solvent and the rate of conversion (compare Michael and Hibbert, *Abstr.*, 1908, ii, 455).

Alkylammonium cyanates have not been obtained hitherto in a pure state; they may be readily prepared, however, by adding the amine to an ethereal solution of cyanic acid at  $-10^\circ$ , except in the case of tripropylamine, triisobutylamine, and triisoamylamine. The salts of primary and secondary amines change into the corresponding substituted carbamides at the ordinary temperature; the rate of change depends largely on the nature of the amine. The following salts were prepared in the manner just described, and analysed; they are white, crystalline substances, and melt in sealed capillary tubes at the temperatures given. *isoAmylammonium cyanate*, m. p.  $49-51^\circ$ ; *diethylammonium cyanate*, m. p. about  $30-32^\circ$ ; *diisobutylammonium cyanate*, m. p.  $53-54^\circ$ ; *piperidine cyanate* softens at  $35-37^\circ$ ; *trimethylammonium cyanate*, and *triethylammonium cyanate*. *Propylammonium cyanate* and *benzylammonium cyanate* are obtained as white precipitates by adding the amine to a solution of cyanic acid in chloroform. *Triisoamylammonium cyanate* is obtained as a thick oil by adding water to the alcoholic solution of the salt formed by shaking a solution of triisoamylammonium chloride in methyl alcohol with silver cyanate at  $-10^\circ$ .

W. H. G.

**Fulminic Acid. II. Two New Methods of Preparation of Fulminic Acid.** HEINRICH WIELAND (*Ber.*, 1909, 42, 820-822. Compare *Abstr.*, 1907, i, 196).—(1) Silver fulminate is formed by treating potassium aminomethylnitrosolate with nitric acid in the presence of silver nitrate. The aminomethylnitrosolic acid is undoubtedly decomposed thus:  $\text{OH}\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{N}_2 + \text{C}\cdot\text{N}\cdot\text{OH}$ .

(2) Methenylamino-oxime, when treated with nitric acid, yields fulminic acid, which in the presence of silver nitrate is obtained as its silver salt. Nitrous oxide, undoubtedly derived from ammonium

nitrate formed during the reaction, is evolved; the methenylaminoxime is decomposed thus:  $\text{CH}(\text{NH}_2):\text{N}\cdot\text{OH} \rightarrow \text{NH}_3 + \text{C}\cdot\text{N}\cdot\text{OH}$ .

W. H. G.

**Nitroacetonitrile.** IV. WILHELM STEINKOPF (*Ber.*, 1909, 42, 617—621).—The constitution of this compound was fully established (*Abstr.*, 1908, i, 327), but experiments to hydrolyse the nitrile to amide were unsuccessful. It is already known that trichloroacetonitrile may be hydrolysed to the corresponding amide (*Abstr.*, 1907, i, 488), and the hydrolysis of the nitroacetonitrile,  $\text{D}^{18} 1.36$ , may be accomplished by passing dry hydrogen chloride through an ethereal solution of nitrile (1 mol.) and methyl alcohol (1 mol.) cooled by a freezing mixture:  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CN} + \text{MeOH} + \text{HCl} \rightarrow [\text{NO}_2\cdot\text{CH}_2\cdot\text{C}(\text{OMe})\cdot\text{NH}, \text{HCl}] \rightarrow \text{NO}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2 + \text{MeCl}$ . The yield is 40%, and the compound so prepared has m. p.  $106-107^\circ$ ; it is, however, identical with nitroacetamide prepared by other methods (compare *Abstr.*, 1905, i, 122, m. p.  $101-102^\circ$ ; Ratz, *Abstr.*, 1904, i, 858, m. p.  $98-99^\circ$ ). This method is recommended as the best method for preparing it.

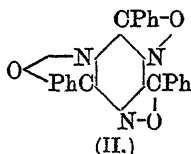
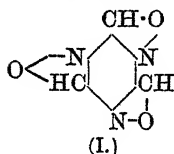
**Dichloronitroacetonitrile**,  $\text{NO}_2\cdot\text{CCl}_2\cdot\text{CN}$ , prepared by the action of chlorine on an ice-cold aqueous solution of ammonium acinitroacetonitrile, is a colourless, heavy oil, b. p.  $39/21$  mm. It decomposes when boiled under atmospheric pressure, is apt to explode if impure under these conditions, and the vapour excites tears.

When an ice-cold solution of ammonium nitroacetonitrile is treated with a concentrated aqueous solution of sodium nitrite, *cyanomethylnitrolic acid*,  $\text{CN}\cdot\text{C}(\text{NOH})\cdot\text{NO}_2$ , is formed as a viscous oil solidifying to a mass of hygroscopic crystals. It is unstable, and forms unstable red ammonium and carmine-red silver salts.

W. R.

**Nitrile Oxides.** II. HEINRICH WIELAND (*Ber.*, 1909, 42, 803—816. Compare *Abstr.*, 1907, i, 527).—It has been shown previously (*Abstr.*, 1907, i, 196) that methylnitrolic acid when warmed with dilute nitric acid decomposes into fulminic and nitrous acids. It is now found that an aqueous solution of methylnitrolic acid when evaporated on a water-bath leaves a residue of carbamide; in this case, nitrous acid is eliminated, and the  $\text{CNOH}$  residue changes into cyanic acid, which then passes into carbamide. It seemed probable that the substance first formed in these reactions was formonitrile oxide, which then underwent transformation into cyanic acid or fulminic acid. The isolation of formonitrile oxide, although not in the unimolecular form, has shown the correctness of this assumption. When an aqueous solution of methylnitrolic acid is treated with the theoretical quantity of a 10% solution of sodium carbonate at very low temperatures, an orange-red solution is obtained, which almost immediately becomes colourless, and deposits a substance having the empirical composition  $\text{CHON}$ . This compound has the properties of the hypothetical formonitrile oxide; thus it yields salts of cyanic acid with alkalis, carbamide with ammonia, phenylcarbamide with aniline, formic acid and hydroxylamine with acids, formic acid and ammonia when reduced with zinc dust and acetic acid, hydrogen cyanide when aluminium amalgam is employed as the reducing agent, and

formhydroxamic acid when treated with water at the ordinary temperature. The physical properties of the substance and its close similarity to trioxymethylene, cyamelide, and cyanuric acid suggest



the constitution represented by formula I. It is proposed to name the substance *trifulmin*; it is obtained as a colourless powder, and is almost as explosive as silver fulminate.

*Tribenzonitrile oxide* (formula II) is prepared from phenylnitrolic acid in the same way as trifulmin. It is a colourless, crystalline substance, m. p. 125–130° (decomp.), and is not so explosive as trifulmin. In its chemical behaviour it is similar to benzonitrile oxide (compare Abstr., 1907, i, 527); thus it is converted by cold alcoholic hydrochloric acid into oxoazoxime hydrochloride to the extent of 80%, whilst the remainder is decomposed into benzoic acid and hydroxylamine. It is converted by aniline into diphenylcarbamide, and when heated in toluene or xylene passes quantitatively into phenylcarbamide.

It is suggested that a nitrile oxide is formed as an intermediate product in Hofmann's reaction, thus:  $R \cdot C(ONa) : N \cdot Br \rightarrow$

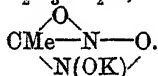
$NaBr + R \cdot \begin{array}{c} O \\ \diagup \quad \diagdown \\ C=N \end{array} \rightarrow O : C : N \cdot R$ . Similarly, in Curtius' azoimide

reaction,  $R \cdot CO \cdot N \cdot \begin{array}{c} N \\ \diagup \quad \diagdown \\ N \end{array} \rightarrow R \cdot \begin{array}{c} O \\ \diagup \quad \diagdown \\ C=N \end{array} + N_2$ .

W. H. G.

**Nitrile Oxides. III. The Salts of Graul and Hantzsch's Leuconitrolic Acid.** HEINRICH WIELAND (*Ber.*, 1909, 42, 816–820. Compare preceding abstract).—Ethynitrolic acid, like the corresponding methyl compound, is decomposed by an aqueous solution of sodium carbonate, yielding *triacetonitrile oxide*,  $C_6H_5O_3N_3$ , obtained as a brittle, vitreous mass, decomposing at about 95°; it is very similar to trifulmin in its chemical properties.

The remainder of the paper contains confirmation of the work of Graul and Hantzsch (Abstr., 1899, i, 187). It is pointed out that the leuco-salts behave as mixtures of triacetonitrile oxide with a nitrite; thus, aniline hydrochloride in aqueous solution is at once diazotised by potassium leuconitrolate; the latter when heated in xylene yields methyl carbimide, and when treated with aniline yields *s*-phenyl-methylcarbamide. It is definitely shown, however, that the leuco-salts are not mixtures; moreover, they have the unimolecular formula  $C_2H_2ON_2M$ , and it is suggested that they have the constitution



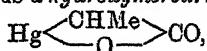
W. H. G.

**Hydroxide and Salts of Mercuriethylenediamine.** LEONE PESCI (*Gazzetta*, 1909, 39, i, 143–147).—Salts of mercuriethylene-diamine,  $Hg \cdot C_2H_4(NH_2)_2$ , are prepared by the action of ethylene-diamine on mercury salts, by boiling ethylenediamine salts with yellow mercuric oxide, or by double decomposition of the acetate. They are

decomposed by hydrogen sulphide, mineral acids, potassium iodide, or sodium thiosulphate.

*Mercuriethylenediamine hydroxide*,  $C_2H_4Hg(NH_2 \cdot OH)_2 \cdot 3.5H_2O$ , prepared from the sulphate and barium hydroxide, forms a white, amorphous powder, decomp.  $128^\circ$ , soluble in water, decomposed by light. The *chloride* crystallises from boiling water, decomp.  $160^\circ$ ; the *sulphate* forms an insoluble precipitate of microscopic, rectangular tablets, containing  $H_2O$ . A preparation known as *sublimina*, containing 43% Hg, appears to contain molecular proportions of this sulphate and of ethylenediamine. The *nitrate* forms microscopic, anhydrous granules, insoluble in water; the *acetate* is also anhydrous, and forms microscopic, hexagonal scales, m. p.  $195^\circ$ . C. H. D.

Synthesis of  $\alpha$ -Hydroxymercuri-fatty Acids. II. Methyl Hydroxymercurimethylmalonate and its Product of Hydrolysis,  $\alpha$ -Hydroxymercuripropionic Anhydride. WALTER SCHOELLER and WALTER SCHRAUTH (*Ber.*, 1909, 42, 777—785. Compare Abstr., 1908, i, 617).—Whereas methyl mercuridimalonate is formed remarkably easily (*loc. cit.*), alkyl-substituted malonates react sluggishly with mercuric oxide. *Methyl  $\alpha$ -hydroxymercurimethylmalonate*,  $OH \cdot Hg \cdot CMe(CO_2Me)_2$ , results when the ester ( $1\frac{1}{4}$  mols.) is shaken with precipitated mercuric oxide (1 mol.) and water for four days at  $37^\circ$  in the dark. Admixed mercuric oxide is removed by careful washing of the product with 1% acetic acid; it decomposes at  $235^\circ$ , and the ester is regenerated by boiling with a halogen acid. *N*-Sodium hydroxide yields  *$\alpha$ -hydroxymercuripropionic anhydride*,



in 97% yield; ammonium sulphide causes blackening, a reaction which appears to be a characteristic of  $\alpha$ -hydroxymercuri-fatty acids;  $\beta$ -acids do not give this reaction. The blue *copper* salt,  $Hg_2C_6H_{10}O_8Cu$ , was analysed; the *calcium*, *lead*, and *mercury* salts are white; the *silver*, yellowish-white. Towards mineral acids it behaves similarly to its lower homologue (*loc. cit.*). Sodium  $\alpha$ -hydroxymercuripropionate is poisonous, "organotrop"; the  $\beta$ -hydroxy-salt is, on the other hand, a disinfectant, "parasitotrop."

Hydroxymercuripropionic anhydride can be obtained in 93% yield from mercury acetamide and methyl methylmalonate in the presence of alkali. The acetamide formed initially from the condensation of mercury acetamide and methyl methylmalonate is soluble in water, whereas that from methyl malonate is not, and as these regenerate the ester with hydrochloric acid, advantage is taken of these facts for the purification of commercial malonic esters. W. R.

So-called Pure  $\Delta^{1,3}$ -Dihydrobenzene and its Molecular Refraction. CARL D. HARRIES and HANS VON SPLAWA-NEYMAN (*Ber.*, 1909, 42, 693—698).—According to Zelinsky and Gorsky (Abstr., 1908, i, 619),  $\Delta^{1,3}$ -cyclohexadiene exhibits no optical exaltation, although it contains conjugate double linkings. Brühl (*ibid.*, ii, 1002) has already questioned the constitution of this compound, and the authors bring forward evidence which indicates that the product

obtained by Crossley's (Trans., 1906, 85, 1403) or Zelinsky's (*loc. cit.*) method is a mixture of  $\Delta^{1,2}$ -cyclohexadiene and cyclohexene.

This evidence is based on the fact that the ozonide of the hydrocarbon when decomposed with acetic acid yields adipindialdehyde as well as succindialdehyde, and from the former, cyclopentenaldehyde (Baeyer and Liebig, Abstr., 1898, i, 638) was readily isolated. J. J. S.

**Sodium Derivative of Indene.** RUDOLF WEISSGERBER (*Ber.*, 1909, 42, 569—572); GESELLSCHAFT FÜR TEERVERWERTUNG (D.R.-P. 205645. Compare Abstr., 1908, i, 873).—Many unsuccessful attempts have been made to obtain the potassium derivative of indene (compare Thiele, Abstr., 1901, i, 182; Kraemer, *ibid.*, 535). It is now found that the sodium derivative,  $C_6H_4 \begin{array}{c} \text{CH} \\ \text{CHNa} \end{array} \text{CH}$ , may be prepared by heating indene with sodamide at 110—115°, by treating indene and sodium at 120—130° with ammonia, or by heating indene with sodium at 140—150°; it is obtained as a brown, amorphous mass having the appearance of colophony. The formation of the sodium derivative of indene furnishes a ready means of obtaining this hydrocarbon in a state of purity from the so-called "heavy benzene," b. p. 175—185°, obtained from coal-tar. This fraction is treated in the manner just described, the unattacked hydrocarbon removed by distillation under reduced pressure, and the sodium indene decomposed with water. W. H. G.

**Indene in Coal Tar.** ADOLF SPILKER and ALFRED DOMBROWSKY (*Ber.*, 1909, 42, 572—573. Compare Kraemer and Spilker, Abstr., 1891, 205).—Pure indene, obtained from coal-tar by the method described in the preceding abstract, has b. p. 182.2—182.4°/761 mm. (corr.),  $D_{20}^{25}$  1.0002,  $n_D^{25}$  1.5773, f. p. -2°. Indene dibromide, contrary to the statement of Kraemer and Spilker (*loc. cit.*), is a stable substance crystallising in colourless, thick prisms, m. p. 31.5—32.5°. W. H. G.

**Photochemical Reactions of the White and Yellow Diphenyl-octatetrenes.** HANS STOBBE (*Ber.*, 1909, 42, 565—568. Compare Abstr., 1908, ii, 339).—From the method of formation, it is probable that the white  $\alpha\beta$ -diphenyl- $\Delta^{\gamma\epsilon\eta}$ -octatetrene of Fichter and Hirsch (Abstr., 1901, i, 594) and the yellow  $\alpha\beta$ -diphenyl- $\Delta^{\gamma\epsilon\eta}$ -octatetrene of Fittig and Batt (Abstr., 1904, i, 744) are stereoisomerides, in which case it should be possible to convert one into the other by the action of light. It is found that both substances in the presence of air and under the influence of light undergo oxidation, yielding resinous products containing benzaldehyde and benzoic acid. In the absence of oxygen, however, only one substance is acted on, namely, the yellow variety, which passes into the white isomeride. W. H. G.

**Photochemical Reactions. IV. Thermodynamic Theory of Photochemical Processes.** FRITZ WEIGERT (*Ber.*, 1909, 42, 850—862. Compare Abstr., 1908, ii, 914).—The photopolymerisation of anthracene to dianthracene has been further studied. The proportionality previously found between the amount of light energy

used chemically and the total energy absorbed by the anthracene is confirmed. From experiments made in the dark at 85° and 105°, the conclusion is drawn that the equilibrium  $2C_{14}H_{10} \rightleftharpoons C_{28}H_{20}$  is altered in favour of the dianthracene at the higher temperature, and the thermal value of the polymerisation is calculated as -20,000 cal. The relation between the equilibrium constant in the dark and temperature is expressed by the equation  $\log K = -4330/T + 10.27$ , which has been tested by experiments at different temperatures in toluene solution, and also in benzene and xylene. The high value of 4.5% has been experimentally found to represent that proportion of the energy absorbed by the anthracene which is used chemically.

When a platinum wire heated electrically is made to glow (temperature about 900°) in a boiling solution of anthracene in ether, or light petroleum, which contains solid anthracene, a crust is formed on the wire. This in part consists of dianthracene.

E. F. A.

**Preparation of Aniline and its Homologues.** AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 204951).—The halogen of chlorobenzene can be replaced by ammonia by heating the halogenated hydrocarbon with ammonia in presence of copper salts. Chlorobenzene (200 parts), 25% aqueous ammonia (600 parts), and copper sulphate (25 parts), when heated at 180–200° for twenty hours, yield 80% of the calculated amount of aniline.

G. T. M.

**Preparation of Sulphanilic Acid.** AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 205150).—Sulphanilic acid in 80% yield can be obtained by heating chlorobenzene-*p*-sulphonic acid with aqueous ammonia and copper chloride at 170° for twelve hours.

G. T. M.

**Action of Calcium Hypochlorite on *m*-Nitroaniline.** WILHELM KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 93–103. Compare Abstr., 1908, i, 523).—By the action of calcium hypochlorite, in such quantity as to contain  $1\frac{1}{2}$  mols. of active chlorine, on 1 mol. of *m*-nitroaniline in glacial acetic acid at 40–60°, allowing the solution to remain for twelve hours, a reddish-brown product is obtained when ice-water is added, and a further brownish-yellow precipitate is obtained on partial neutralisation of the filtrate.

The first product consists mainly of 2:6-dichloro-3-nitroaniline, long needles, m. p. 110.8°. The *acetyl* derivative forms glistening crystals, m. p. 128.6°. Together with this is the 2:4:6-trichloro-3-nitroaniline, m. p. 102.5°, the *acetyl* derivative has m. p. 194–195°, and also 2:4-dichloro-3-nitroaniline, m. p. 97.5°, *acetyl* derivative has m. p. 128.9°.

The second fraction contains chiefly 4-chloro-3-nitroaniline, m. p. 97.6°; *acetyl* derivative, m. p. 150°. No trace of 4:6-dichloro-3-nitroaniline could be detected.

C. H. D.

[Preparation of the Alkali Derivatives of Aromatic Primary and Secondary Amines.] BASLER CHEMISCHE FABRIK (D.R.-P. 205493).—The aromatic amines do not react readily with the alkali

metals, but it has now been found that when a mixture of alkali metal and an alkali hydroxide is employed, the reaction proceeds smoothly.

A mixture of metallic sodium and potassium hydroxide heated to 200—260° was employed, and at these temperatures aniline, *o*-toluidine, and methylaniline were readily absorbed, forming mixtures of their sodium and potassium derivatives, which were thus obtained as crystalline, dark brown, very reactive products, regenerating the base on treatment with water. G. T. M.

**Mercury Double Salts of Tetrahydronaphthylamines.** OSKAR GROHMANN and ARJEN BROUWER (*Annalen*, 1909, 365, 50—52. Compare Bamberger, *Abstr.*, 1888, 600, 960).—*ac*- $\beta$ -Tetrahydronaphthylamine hydrochloride combines with mercuric chloride in two proportions. The one compound,  $C_{10}H_{11}\cdot NH_2\cdot HCl, 2HgCl_2$ , crystallises from water in long, glistening prisms, m. p. 241.5—242°; the other,  $2(C_{10}H_{11}\cdot NH_2\cdot HCl), HgCl_2$ , crystallises in colourless plates, m. p. 221—222°, and is only formed in the presence of an excess of hydrochloric acid. When crystallised from water it yields the less fusible compound.

*ar*- $\alpha$ -Tetrahydronaphthylamine yields the compound

$C_{10}H_{11}\cdot NH_2\cdot HCl, HgCl_2$ , m. p. 179—180°; also a compound,  $2(C_{10}H_{11}\cdot NH_2\cdot HCl), HgCl_2$ , which crystallises in doubly refracting plates, m. p. 217.5—219°, and a third compound,  $C_{10}H_{11}\cdot NH_2\cdot HCl, 2HgCl_2$ , which forms colourless, prismatic needles, m. p. 192.5—193.5°. J. J. S.

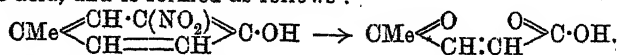
**Preparation of 2-*p*-Nitrosoanilinonaphthalene-6 : 8-disulphonic Acid.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205414).—When treated with alcoholic, or concentrated aqueous, hydrochloric acid the nitrosamines of the 2-arylamino-naphthalenes are converted into nitroso-derivatives containing the nitroso-group in the contiguous  $\alpha$ -position of the naphthalene nucleus. When the nitrosamine of 2-anilinonaphthalene-6 : 8-disulphonic acid is thus treated, the nitroso-group migrates into the phenyl ring in the para-position to the aminic nitrogen, forming 2-*p*-nitrosoanilinonaphthalene-6 : 8-disulphonic acid,  $NO_2\cdot C_6H_4\cdot NH\cdot C_{10}H_5(SO_3H)_2$ , reddish-brown needles, readily soluble in water. G. T. M.

**The Compounds which Cause the Red Colour in Phenol.** HARRY D. GIBBS (*Philippine J. Sci.*, 1908, A, 3, 361).—Phenol, which had become red by exposure to sunlight at a temperature of 30°, was treated with a small quantity of sulphurous acid and distilled in steam; the residue in the distillation flask, after filtration from a very small amount of red precipitate, was extracted with ether, and found to contain considerable quantities of catechol and quinone. The red colour is attributed to the solution in phenol of quinone and the highly-coloured condensation product phenoquinone. The presence of oxygen was proved to be necessary for the production of the red colour, since no coloration was produced in moist phenol contained in sealed tubes filled with carbon dioxide on exposure to

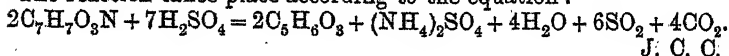
sunlight. This fact, moreover, appears to show that water and carbon dioxide do not react in the presence of sunlight to form hydrogen peroxide and oxygen, as assumed by von Baeyer, since the presence of oxygen in these experiments would have been revealed by the production of a red colour. P. H.

**Preparation of *p*-Aminophenol and its *N*-Alkyl Derivatives.** AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 205415).—By heating *p*-chlorophenol at 135–140° with ammonia or primary bases (such as methylamine) in the presence of copper salts (copper sulphate, for example), *p*-aminophenol, *p*-methylaminophenol and similar compounds are readily obtained in excellent yield. *p*-Ethylaminophenol, white needles, m. p. 100°, which is thus obtained, gives an oily nitroso-compound. G. T. M.

**Behaviour of 3-Nitro-*p*-cresol towards Sulphuric Acid.** GUSTAV SCHULTZ and OSKAR LÖW (*Ber.*, 1909, 42, 577–578).—The compound obtained by the action of fuming sulphuric acid on 3-nitro-*p*-cresol, previously thought to have the formula  $C_7H_5O_4$  (Schultz, *Abstr.*, 1907, i, 1030), has now been found to be identical with acetylacrylic acid, and is formed as follows:



The reaction takes place according to the equation:



J. C. C.

**Intramolecular Transformations of Acylated Compounds.** KARL AUWERS (*Annalen*, 1909, 364, 147–182).—The results obtained in this investigation, together with those published previously on the intramolecular transformations of acylated phenols containing amino- and imino-groups (compare Auwers, *Abstr.*, 1904, i, 581, 736, 1051; Auwers and Bondy, *ibid.*, 1053; Auwers and Bürger, *ibid.*, 1054; Auwers and Dannehl, *Abstr.*, 1908, i, 458), are discussed in detail, and the following conclusions drawn: (1) In ordinary circumstances an acyl group migrates spontaneously from the oxygen to the nitrogen, no matter whether this be the first, second, or third member of a side-chain in the ortho-position, provided the acid character of the acyl group and the basic character of the nitrogen group are sufficiently pronounced. (2) The migration of the acyl group is rendered more difficult by greatly diminishing the basic character of the amino- or imino-group; in many cases a rearrangement is totally prevented. (3) The migration of the acyl group is similarly affected by reducing the acidic character of the acid radicle, but up to the present no case has been observed where the migration has been completely checked. (4) The nitrogen group is able to attract both heavy and light acid radicles, provided its basic character is sufficiently pronounced. The relative weight of the acyl group is, however, a determinative factor in the intramolecular transformation when the compound is a neutral substance, or only slightly basic; as a rule, in such cases, the ease with which the acyl group migrates diminishes greatly with an increase in the weight of the group.

[With KARL MÜLLER.]—*p*-Tolyl methyl ether and chloroacetyl chloride react in equivalent proportions in the presence of aluminium chloride, yielding 3-chloroacetyl-*p*-cresol and 3:5-dichloroacetyl-*p*-cresol (compare Fries and Finck, this vol. i, 42). 3:5-Diacetyl-*p*-cresol,  $C_{11}H_{12}O_3$ , is obtained when 3 mols. of chloroacetyl chloride are employed; it crystallises in slender needles and long, compact prisms, m. p. 82—83°. 3-Chloroacetyl-*p*-cresol, when reduced with zinc dust and acetic acid, yields 3-acetyl-*p*-cresol, long, glistening, colourless prisms, m. p. 50° (compare Auwers and Betteridge, Abstr., 1900, ii, 262), and when heated with benzoyl chloride yields the *benzoate*,  $C_{16}H_{18}O_3Cl$ , long, glistening prisms, m. p. 92°. The latter substance, when heated with aniline or *p*-toluidine dissolved in toluene, yields

*N*-benzoyl-3-phenylglycyl-*p*-cresol,  $\begin{array}{c} CH-CH_3 \\ | \\ CH \cdot C(OH) : C \cdot CO \cdot CH_2 \cdot NPhBz \end{array}$ , pearly

scales, m. p. 172.5°, and *N*-benzoyl-3-*p*-tolylglycyl-*p*-cresol,  $C_{23}H_{21}O_3N$ , silvery leaflets; m. p. 193.5°; the *oxime* of the former,  $C_{23}H_{20}O_3N_2$ , forms flat, compact needles, m. p. 157—158°. 3-Phenylglycyl-*p*-cresol,  $C_{15}H_{15}O_2N$ , obtained by boiling 3-chloroacetyl-*p*-cresol with an alcoholic solution of aniline, crystallises in small, slightly yellow needles, m. p. 82—83°; it yields the *N*-benzoyl derivative, m. p. 172.5°, even when benzoylated in pyridine.

[With HUGO DANNEHL.]—When the acetate of dibromo-*p*-hydroxybenzyl bromide is heated with *p*-nitrophenylhydrazine under pressure at 100°, it yields the  $\alpha$ -*N*-acetate of dibromo-*p*-hydroxybenzyl-*p*-nitrophenylhydrazine,  $OH \cdot C_6H_4Br_2 \cdot CH_2 \cdot NAc \cdot NH \cdot C_6H_4 \cdot NO_2$ , a chocolate-brown, crystalline substance, m. p. 258—259° (decomp.); the same compound is obtained by condensing *s*-acetyl-*p*-nitrophenylhydrazide with dibromo-*p*-hydroxybenzyl bromide.

[With FRITZ EISENLOHR.]—The phenylurethane of 3-nitro-*p*-cresol,  $NO_2 \cdot C_6H_4Me \cdot O \cdot CO \cdot NHPh$ , is obtained by heating the nitrocresol with phenylcarbimide under pressure at 120—130°; it forms pale yellow crystals, m. p. 102°, and when reduced with zinc dust and acetic acid yields *O*-carbanilido-3-amino-*p*-cresol,  $C_{14}H_{14}O_2N_2$ , white crystals, m. p. 169°, and *N*-carbanilido-3-amino-*p*-cresol,  $C_{14}H_{14}O_2N_2$ ; the latter substance may also be prepared by the action of phenylcarbimide on 3-amino-*p*-cresol, or by treating the *O*-derivative with hot glacial acetic acid; it crystallises in slender, silky needles, m. p. 158—159°.

[With W. HIRT and KARL MÜLLER.]—3-Benzeneazo-*p*-tolyl propionate,  $C_{16}H_{16}O_3N_2$ , obtained by the action of propionyl chloride on 3-benzeneazo-*p*-cresol, forms small, bright red needles, m. p. 48—49°, and is reduced by sodium amalgam to the corresponding hydrazo-derivative,  $C_{16}H_{18}O_3N_2$ , a green powder, m. p. 100° (decomp.).

*p*-Tolueneazo-*p*-tolyl propionate,  $C_{17}H_{18}O_3N_2$ , can only be obtained by heating the azo-phenol with propionic anhydride; it crystallises in dark red leaflets, m. p. 62°, and when reduced yields the corresponding hydrazo-derivative,  $C_{17}H_{20}O_3N_2$ , obtained as colourless leaflets, m. p. 105°. Both of the preceding hydrazo-compounds are definitely shown to be *O*-propionates.

Dibromo-*o*-propionybenzyl bromide,  $C_{10}H_9O_2Br_3$ , forms white, felted needles, m. p. 89°, and when acted on by phenylhydrazine yields

the  $\alpha$ -N-propionyl-3:5-dibromo-2-hydroxybenzylphenylhydrazine,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{N}(\text{COEt})\cdot\text{NHPh}$ , pearly leaflets, m. p.  $164^\circ$ ; the same compound is obtained by the action of *s*-propionylphenylhydrazine on dibromo-*o*-hydroxylbenzyl bromide. Dibromo-*o*-propionoxybenzyl bromide, when treated with *s*-acetylphenylhydrazine, yields the *o*-propionate of  $\alpha$ -N-acetyldibromo-*o*-hydroxybenzylphenylhydrazine,  $\text{C}_{18}\text{H}_{18}\text{O}_5\text{N}_2\text{Br}_2$ , crystallising in glistening leaflets, m. p.  $188$ – $189^\circ$ . The substance is not affected by boiling with glacial acetic acid.

W. H. G.

**Crystallography of *p*-Dithymolylamine Dimethyl Ether.** A. FERSMANN (*Zeitsch. Kryst. Min.*, 1909, 43, 219; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 133–138).—The crystals are rhombic [ $a:b:c=1:152:1:0\cdot685$ ] (compare Decker and Solonina, *Abstr.*, 1905, i, 197).

L. J. S.

**Separation of *o*- and *p*-Phenolsulphonic Acids.** JULIUS OBERMILLER (D.R.-P. 202168).—A solution of *o*- and *p*-phenolsulphonic acids is treated with barium carbonate and evaporated until granular aggregates of barium *o*-phenolsulphonate separate, accompanied by needles of the para-salt. The latter is dissolved by the cautious addition of water, and the less soluble ortho-salt thus separated. The mother liquor is treated with magnesium sulphate and evaporated until magnesium *p*-phenolsulphonate separates. The final mother liquor contains a little of the meta-isomeride and more of the ortho-salt.

When the free acids are converted into magnesium salts and their solutions evaporated, the major portion of the para-salt separates first. Further addition of magnesia to the mother liquor leads to separation of the dimagnesium salt of the ortho-acid.

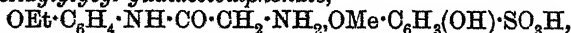
G. T. M.

**Preparation of *p*-Aminophenol-2-sulphonic Acid.** AKTIENGESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 202566).—*p*-Aminophenol-2-sulphonic acid is prepared by heating 4-chlorophenol-2-sulphonic acid with aqueous ammonia and copper chloride at  $165^\circ$ .

G. T. M.

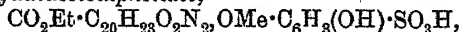
**New Salts of Guaiacolsulphonic Acid.** ACHILLE TAGLIAVINI (*Boll. chim. farm.*, 1909, 48, 6–9).—Potassium guaiacolsulphonate is used as a drug; salts have now been prepared with antipyretic and analgesic bases.

*p*-Phenetidylglycyl guaiacolsulphonate,



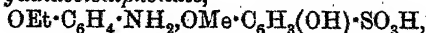
prepared by adding an ethereal solution of the base to a concentrated alcoholic solution of the acid, forms small crystals, m. p.  $183^\circ$ .

*Equinine guaiacolsulphonate,*



prepared by mixing hot solutions of basic equinine sulphate and barium guaiacolsulphonate, forms a powder, m. p.  $84^\circ$ .

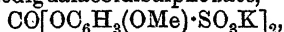
*p*-Phenetidine guaiacolsulphonate,



prepared similarly to the first salt mentioned, forms microscopic crystals, m. p. 186—188°.  
C. H. D.

**Preparation of Salts of Carbonatoguaiacol-mono- and -disulphonic Acids.** ALFRED EINHORN (D.R.-P. 203754).—It has been found that carbonyl chloride will condense with alkali guaiacol-sulphonates in alkaline solution, giving derivatives in which the carbonyl group becomes attached to two phenolic oxygens.

Potassium carbonatodiguaiacoldisulphonate,



needles from water, is produced by passing carbonyl chloride into an alkaline solution of potassium guaiacolsulphonate (thiocol). Potassium carbonatodiguaiacolsulphonate,  $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{O}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{SO}_3\text{K}$ , is similarly obtained from a mixture of guaiacol and its sulphonate.

G. T. M.

**2-Hydroxystilbene.** STANISLAUS VON KOSTANECKI and JOSEF TAMBOUR (*Ber.*, 1909, 42, 825—827).—2-*Hydroxystilbene*, prepared from 2-methoxystilbene by heating with alcoholic potassium hydroxide at 160°, crystallises in colourless needles, m. p. 147°, which dissolve in dilute sodium hydroxide with a green fluorescence; 2-*acetoxystilbene* forms colourless needles, m. p. 54—55°.

2-*Acetoxystilbene dibromide*,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHPhBr}$ , prepared by the addition of bromine in carbon disulphide solution, separates in long, glistening needles, m. p. 150°. When heated with sodium ethoxide, it is converted into the 1-phenylcoumarone,  $\text{C}_6\text{H}_4\langle\overset{\text{O}}{\text{CH}}\rangle\text{CPh}$ , m. p. 120—121°, described by Stoermer (*Abstr.*, 1904, i, 181).

2-*Stilbenyloxyacetic acid*,  $\text{CHPh}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises in long needles, m. p. 136°; the *dibromide* forms colourless needles, m. p. 188° (decomp.).

*Ethylene di-2-stilbenyl ether*,  $\text{C}_2\text{H}_4(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHPh})_2$ , formed by the action of ethylene bromide on an alcoholic solution of sodium-*o*-hydroxystilbene, crystallises in colourless needles, m. p. 110°.

E. F. A.

**Preparation of Anthranol and its Derivatives from the Corresponding Anthraquinones by Reduction with Metals and Acid.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 201542).—Anthranol is readily obtained by adding copper or aluminium powder to a solution of anthraquinone in concentrated sulphuric acid at 30—40°, and pouring the decolorised solution into water; it is recrystallised from glacial acetic acid containing a trace of aluminium and a little hydrochloric acid.

$\alpha$ -Aminocanthranol can be similarly prepared from  $\alpha$ -aminocanthraquinone by reduction with aluminium bronze in cold concentrated sulphuric acid.

G. T. M.

**Diisoeugenol.** ERNESTO PUXEDDU (*Gazzetta*, 1909, 39, i, 131—137).—Whilst isoeugenol and similar compounds containing the allyl group readily polymerise, the isomerides containing the propenyl group do not yield polymerides. *iso*Eugenol is best etherified by treatment

with sodium hydroxide and ethyl sulphate; the ethyl ether forms brilliant scales, m. p.  $64^{\circ}$  (compare Eykman, Abstr., 1890, 748). The molecular weight in acetic acid solution is normal. Dry hydrogen chloride in ethereal solution converts it into a polymeride crystallising from aqueous alcohol in white prisms, m. p.  $130^{\circ}$ . The polymeride obtained by Wassermann (Abstr., 1879, 790) had a lower m. p. and was insoluble in ether, whereas the new compound dissolves readily in ether. It is insoluble in water, dilute acids, or aqueous alkalis.

Diisoeugenol is best prepared by heating an alcoholic solution of isoeugenol with fuming hydrochloric acid on the water-bath. It forms white needles, m. p.  $180^{\circ}$ . Ethyl sulphate or iodide converts its sodium derivative into an ethyl ether identical with that obtained by the direct polymerisation of isoeugenol ethyl ether.

The nature of the isomerism of the two diethyl ethers is not yet certain. The products of bromination and oxidation are under investigation. C. H. D.

**Polymerisation of Aromatic Ethylenic Compounds.** LUIGI FRANCESCONI and ERNESTO PUXEDDU (*Gazzetta*, 1909, 39, i, 202—211).—Although compounds in which the side-chain contains a pair of doubly-linked carbon atoms, one of which is directly joined to the benzene ring, generally polymerise, there are great differences in the readiness with which polymerisation takes place in related compounds. The authors have studied the influence of constitution in the case of eugenol and isoeugenol and their ethers, and of safrole and isosafrole.

Diisoeugenol is obtained when light acts on an alcoholic solution of isoeugenol in presence of hydrochloric acid, or by the action of hydrogen chloride on the dry ethereal solution (compare Puxeddu, preceding abstract). The product is in all cases identical with that obtained by Tiemann (Abstr., 1892, 45) by the hydrolysis of the acetyl derivative.

Eugenol and safrole do not polymerise when treated by either method. isosafrole yields a viscous product.

Diisoeugenol dimethyl ether crystallises from aqueous alcohol in long, white needles, m. p.  $106^{\circ}$ .

Bromine reacts with diisoeugenol in chloroform solution, yielding a dibromo-derivative, m. p.  $168^{\circ}$ , which on analysis did not give figures corresponding with any simple formula.

Bromine converts diisoeugenol dimethyl ether in ethereal solution into a monobromo-derivative,  $C_{23}H_{27}O_4Br$ , crystallising from alcohol, m. p.  $125^{\circ}$ . C. H. D.

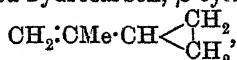
### Cyclic Trimethylene Compounds of the Type $RHC \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix}$

PIERRE BRUYLANTS (*Bull. Acad. roy. Belg.*, 1908, 1011—1084).—The author has prepared a series of compounds containing the cyclopropyl group, and has recorded in a series of tables the relations obtaining between the boiling points and densities of these compounds and the corresponding isopropyl and allyl derivatives. The compounds examined include: (1) ketones of the type  $R \cdot CO \cdot CH \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix}$ , obtained by

the action of organomagnesium derivatives on ethylenoacetonitrile (*cyclopropanecarboxylonitrile*),  $\text{NC}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ ; (2) the secondary alcohols,  $\text{OH}\cdot\text{CHR}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , prepared from the ketones by reduction; (3) the tertiary alcohols,  $\text{OH}\cdot\text{CRR}'\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , prepared by applying the Grignard reaction to the ketones; (4) the chlorides, bromides, iodides, and acetates of the tertiary alcohols; (5) the ethers and unsaturated hydrocarbons obtained from these salts.

*cycloPropyl methyl ketone*,  $\text{COMe}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$  (Perkin, *Trans.*, 1885, 835; Lipp, *Abstr.*, 1889, 843), prepared by the action of magnesium methyl bromide on *cyclopropanecarboxylonitrile*, has b. p.  $114^\circ/772$  mm. *cycloPropyl ethyl ketone*,  $\text{COEt}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , b. p.  $132-133^\circ$  (corr.)/ $767$  mm.,  $D^{20}$  0.9152,  $n_D^{20}$  1.42931, on reduction with sodium and alcohol yields *cyclopropylethylcarbinol*,  $\text{OH}\cdot\text{CHEt}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , b. p.  $140^\circ/767$  mm.,  $D^{20}$  0.8901,  $n_D^{20}$  1.4326; the *acetate* has b. p.  $159^\circ/765$  mm.,  $D^{20}$  0.8175. *cycloPropyl isopropyl ketone*,  $\text{COPr}^\beta\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , b. p.  $139-141^\circ/769$  mm.,  $D^{20}$  0.9006,  $n_D^{20}$  1.42731, yields on reduction *cyclopropylisopropylcarbinol*,  $\text{OH}\cdot\text{CHPr}^\beta\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , b. p.  $151-152^\circ/769$  mm.,  $n_D$  1.43643; the *acetate* has b. p.  $171-173^\circ$ .

*cycloPropyldimethylcarbinol*,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$  (Zelinsky, *Abstr.*, 1901, i, 661; 1902, i, 70), prepared by the action of magnesium methyl bromide on ethyl *cyclopropanecarboxylate*, has b. p.  $124^\circ/776$  mm.,  $D^{20}$  0.9335,  $n_D^{20}$  1.43232; the *chloride* has b. p.  $132-133^\circ$ ,  $D^{20}$  0.9441; the *bromide* has b. p.  $152-153^\circ/766$  mm.,  $D^{20}$  1.218; the *iodide* has b. p.  $113-114^\circ/55$  mm.,  $D^{20}$  1.338; the *acetate* has b. p.  $159-160^\circ$ ,  $D^{20}$  0.9167. The unsaturated hydrocarbon,  $\beta$ -*cyclopropylpropylene*,



b. p.  $77^\circ/758$  mm.,  $D^{20}$  0.7375,  $n_D^{20}$  1.45037, is obtained advantageously by the action of dry potassium hydroxide on the preceding bromide at  $170^\circ$ ; it is also produced by the action of alcoholic potassium hydroxide on the chloride, bromide, or iodide, or by the direct dehydration of the alcohol by means of phosphoric oxide, and combines with bromine to form the *tribromo-derivative*,  $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CBr}\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ . 1-Ethoxy-

1-isopropylcyclopropane,  $\text{CH}_2\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH} \end{smallmatrix}\text{CPr}^\beta\cdot\text{OEt}$ , b. p.  $140-145^\circ$ ,  $D^{20}$  0.82493,  $n_D^{20}$  1.42481, is formed together with the preceding hydrocarbon when *cyclopropyldimethylcarbinol* is heated with alcohol at  $100^\circ$ , or by the action of alcoholic potassium hydroxide on its bromide, chloride, or

iodide; it reacts with hydrobromic acid to form 1-bromo-1-isopropyl-cyclopropane,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CPr}^i\text{Br}$ , b. p.  $174^\circ$  or  $108\text{--}110^\circ/55$  mm.,  $D^{20}_D$  1.1597, which is isomeric with the bromide of the original alcohol.

cycloPropyldiethylcarbinol,  $\text{OH}\cdot\text{CEt}_2\cdot\text{CH}\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ , has b. p.  $158\text{--}159^\circ/759$  mm.,  $D^{20}_D$  0.9055,  $n^{20}_D$  1.44638; the *chloride* has b. p.  $160\text{--}166^\circ$ ,  $D^{20}_D$  0.9407; the *bromide* has b. p.  $186\text{--}187^\circ/756$  mm.,  $D^{20}_D$  1.1479; the *iodide* has b. p.  $152^\circ/55$  mm.,  $D^{20}_D$  1.3357; when the bromide is heated with alcoholic potassium hydroxide, a mixture of the ethylenic hydrocarbon,  $\text{CHMe}\cdot\text{CEt}\cdot\text{CH}\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ ,  $\gamma$ -cyclopropyl- $\Delta^3$ -amylene, and the ether,  $\text{CHEt}_2\cdot\text{C}(\text{OEt})\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$  ( $\beta$ -ethyl- $\alpha$ -ethyleno- $\alpha$ -ethoxybutane), is produced; the hydrocarbon has b. p.  $129\text{--}130^\circ$ ,  $D^{20}_D$  0.7644,  $n^{20}_D$  1.45841, and the ether has b. p.  $176\text{--}178^\circ$ ,  $D^{20}_D$  0.8130.

cycloPropylmethylethylcarbinol,  $\text{OH}\cdot\text{CMeEt}\cdot\text{CH}\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ , has b. p.  $141\text{--}142^\circ/761$  mm.,  $D^{20}_D$  0.90119,  $n^{20}_D$  1.44135; the *chloride* has b. p.  $150\text{--}153^\circ$ ,  $D^{20}_D$  0.9391; the *bromide* has b. p.  $167\text{--}168^\circ/766$  mm.,  $D^{20}_D$  1.1938; the *iodide* has b. p.  $128\text{--}130^\circ/55$  mm.,  $D^{20}_D$  1.3499. The ethylenic hydrocarbon,  $\text{CHMe}\cdot\text{CMe}\cdot\text{CH}\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$  ( $\beta$ -cyclopropyl- $\Delta^3$ -amylene), is obtained from the preceding bromide by the action of potassium hydroxide at  $170^\circ$ , and has b. p.  $107\text{--}109^\circ/764$  mm.,  $D^{20}_D$  0.7743,  $n^{20}_D$  1.44476. M. A. W.

Action of Sodium and Amyl Alcohol on Cholesterol. G. G. WILENKO and SIGMUND MORTYLEWSKI (*Bull. Acad. Sci. Cracow*, 1908, 837—841. Compare Diels and Abderhalden, *Abstr.*, 1906, i, 272; Neuberg, *ibid.*, 356; Windaus, *ibid.*, 1907, i, 610).—In addition to dihydrocholesterol two new products have been obtained by reducing cholesterol with sodium and boiling amyl alcohol. One of these resembles coprosterol, and is termed *l-coprosterol*. Of the three compounds it is the one most readily soluble in ethyl alcohol, and crystallises in long needles, m. p.  $86\text{--}87^\circ$ . It has  $[\alpha]_D -14.3^\circ$ , and gives most of the colour reactions characteristic of ordinary coprosterol. The third product, termed  $\gamma$ -cholesterol,  $\text{C}_{27}\text{H}_{46}\text{O}$ , is sparingly soluble in ethyl alcohol, and crystallises in glistening, rhombic plates, m. p.  $135\text{--}137^\circ$ . Some specimens were dextro-rotatory, others inactive. It yields an *acetate*, m. p.  $100\text{--}102^\circ$ , but does not form an additive compound with bromine. The best yields of  $\gamma$ -cholesterol are obtained when the reduction is carried out at  $110\text{--}115^\circ$ . Higher temperatures favour the formation of *l-coprosterol*. J. J. S.

Phytosterol from Rape Seed Oil. ADOLF WINDAUS and A. WELSCH (*Ber.*, 1909, 42, 612—616. Compare Windaus and Hauth, *Abstr.*, 1907, i, 129, 921).—The phytosterol from rape seed oil, like

phytosterols from other sources, is a mixture of a stigmasterol and a sitosterol, which may be separated by the action of bromine on the mixture of acetyl derivatives. The stigmasterol yields a compound,  $C_{30}H_{48}O_2Br_4$ , analogous to stigmasteryl acetate tetrabromide. This is termed *brassicasteryl acetate tetrabromide*, and crystallises from a mixture of chloroform and alcohol in well-developed, rhombic plates, which decompose at  $209^\circ$ .

*Brassicasteryl acetate*,  $C_{30}H_{48}O_2$ , obtained by the action of zinc dust and acetic acid on the tetrabromide, crystallises from alcohol in thin, six-sided plates, m. p.  $157-158^\circ$ . When hydrolysed with alcoholic potash it yields *brassicasterol*,  $C_{28}H_{46}O, H_2O$ , which also crystallises from alcohol in six-sided plates, m. p.  $148^\circ$ . It loses the water of hydration at  $100^\circ$ , and has  $[\alpha]_D^{18} - 64^\circ 25'$  in chloroform and  $-63^\circ 31'$  in ether; the *propionate*,  $C_{31}H_{50}O_2$ , has m. p.  $132^\circ$ , and yields a *tetrabromide* which decomposes at  $206^\circ$ . The *benzoate* crystallises from alcohol in long, glistening needles, m. p.  $167^\circ$ .

The sitosterol can be obtained from the mother liquors of the stigmasterol tetrabromide in the form of its dibromide. The sitosterol has m. p.  $142^\circ$  and  $[\alpha]_D^{20} - 34^\circ 20'$  in ether. The acetate has m. p.  $134^\circ$ ; propionate,  $116^\circ$ ; cinnamate,  $151^\circ$ , and benzoate,  $143^\circ$ .

J. J. S.

**Preparation of Crystalline Salts of *o*-Dihydroxyphenylethanolmethylamine.** FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 202169. Compare Abstr., 1908, i, 418).—*o*-Dihydroxyphenylethanolmethylamine hydrochloride, colourless crystals, m. p.  $157^\circ$ , was prepared by adding alcoholic hydrochloric acid to synthetically prepared *o*-dihydroxyphenylethanolmethylamine moistened with absolute alcohol.

G. T. M.

**Crystallography of 2-Methylcyclohexyl Benzoate.** MISS E. D. REVUTZKY (*Zeitsch. Kryst. Min.*, 1909, 46, 218; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 139–141).—The crystals are rhombic  $[a:b:c = 0.9460:1:0.7811]$ .

L. J. S.

**Preparation of Acyl Derivatives of the Esters of the Aminohydroxy-acids.** LES ÉTABLISSEMENTS POULENC FRÈRES (D.R.-P. 202167. Compare Abstr., 1908, i, 937).—The acylation of the alkyl esters of the aminohydroxy-acids must be effected in the absence of strong alkalis in order to avoid hydrolysis of the ester group.

*Ethyl  $\beta$ -dimethylamino- $\alpha$ -benzoyloxyisobutyrate*,  
 $NMe_2 \cdot CH_2 \cdot CMe(OBz) \cdot CO_2Et$ ,

was obtained in the form of its *hydrochloride*, needles, m. p.  $137^\circ$ , by mixing cold benzene solutions of benzoyl chloride and ethyl dimethylaminohydroxyisobutyrate; the *base* is a syrup, b. p.  $210^\circ/42$  mm. The *methyl* and *amyl* esters are prepared similarly; their hydrochlorides melt at  $149-150^\circ$  and  $134^\circ$  respectively; the corresponding bases boil at  $220^\circ/75$  mm. and  $213^\circ/27$  mm. The patent contains descriptions of six other similar esters.

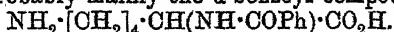
G. T. M.

**Synthesis of Inactive Lysine from Piperidine.** JULIUS VON BRAUN (*Ber.*, 1909, 42, 839–846).—The opening of the piperidine

ring by means of phosphorus chloride has been made use of for the synthesis of cadaverine, pimelic acid, and  $\epsilon$ -leucine (Abstr., 1904, i, 918, 970, 1019; 1907, i, 524). Amongst the products of this reaction are two, namely,  $\epsilon$ -phenoxyhexonitrile,  $C_6H_5O \cdot [CH_2]_5 \cdot CN$ , and benzoyl- $\epsilon$ -leucinenitrile,  $COPh \cdot NH \cdot [CH_2]_5 \cdot CN$ , which contain the skeleton of lysin. The corresponding phenoxyhexoic acid forms a compound,  $C_6H_4Br \cdot O \cdot [CH_2]_5 \cdot CHBr \cdot CO_2H$ , m. p.  $105^\circ$ , in which the  $\alpha$ -bromine atom can be replaced by  $NH_2$ , but the elimination of the brominated phenyl group by bromine could not be carried out. On the other hand,  $\epsilon$ -benzoylaminohectic acid can be brominated in the  $\alpha$ -position, the bromine replaced by  $NH_2$ , and the benzoyl group eliminated, giving inactive lysine.

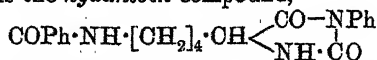
$\epsilon$ -Benzoylaminohectic acid,  $COPh \cdot NH \cdot [CH_2]_5 \cdot CO_2H$ , is obtained, on hydrolysing the nitrile with potassium hydroxide under special precautions, in long, colourless needles, m. p.  $79^\circ$ . It decomposes when distilled, even in a vacuum, forming benzoic acid and the  $\epsilon$ -lactam,  $NH \cdot [CH_2]_5 \cdot CO$ . When brominated in presence of phosphorus a con-

siderable excess of bromine is required. Apparently the imide bromide complex,  $C_6H_5 \cdot CBr \cdot NX$ , is formed at the same time as the  $\alpha$ -carbon is brominated, but the complex is destroyed on adding water.  $\alpha$ -Bromo- $\epsilon$ -benzoylaminohectic acid,  $COPh \cdot NH \cdot [CH_2]_4 \cdot CHBr \cdot CO_2H$ , forms a mass of colourless needles, m. p.  $166^\circ$ . It reacts with aqueous ammonia at  $0^\circ$ , forming  $\alpha$ -amino- $\epsilon$ -benzoylaminohectic acid, m. p.  $268^\circ$  when heated quickly, m. p.  $263^\circ$  when slowly heated. The monobenzoyllysine described by Fischer and Weigert (Ber., 1902, 35, 3772) was probably mainly the  $\alpha$ -benzoyl compound,



Inactive lysine, obtained by heating benzoyllysine with excess of hydrochloric acid for several hours under pressure at  $115^\circ$ , is in all respects identical with the product obtained by Fischer and Weigert (*loc. cit.*).

Characteristic is the *hydantoin* compound,



By the action of phenylcarbimide on  $\epsilon$ -benzoyllysine the *hydantoic acid*,  $COPh \cdot NH \cdot [CH_2]_4 \cdot CH(NH \cdot CO \cdot NHPh) \cdot CO_2H$ , is first formed as a grey mass. This is warmed with concentrated hydrochloric acid and converted into the *hydantoin*, crystallising in matted needles, m. p.  $156^\circ$ .

E. F. A.

**Preparation of *o*-Nitrobenzonitrile and *o*-Nitrobenzamide.** KALLE & Co. (D.R.-P. 204477).—When *o*-nitrobenzaloxime is warmed with dilute aqueous sodium carbonate for nine hours, it yields *o*-nitrobenzamide together with a small amount of *o*-nitrobenzoic acid. When heated with a weak solution of potassium cyanide for nine hours, this oxime furnishes *o*-nitrobenzonitrile with small quantities of *o*-nitrobenzamide and *o*-nitrobenzoic acid. G. T. M.

**Preparation of 2-Nitro-4-aminobenzoic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 204884).—2-Nitro-4-amino-

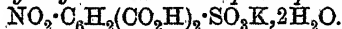
*benzoic acid*, yellowish-brown crystals, m. p. 234—235°, has now been obtained by reducing 2 : 4-dinitrobenzoic acid with sodium sulphide at 90° in the absence of alkalis. G. T. M.

**Oxidation Products of 6-Nitro-1 : 3-dimethylbenzene-4-sulphonic Acid.** WILLIAM J. KARSLAKE and P. A. BOND (*J. Amer. Chem. Soc.*, 1909, 31, 405—410).—Potassium 6-nitro-1 : 3-xylene-4-sulphonate has been prepared by a modification of Claus and Schmidt's method (*Abstr.*, 1886, 708). When this salt is oxidised with cold alkaline solution of potassium permanganate, the following three products are obtained.

(1) *Potassium 4-nitro-2-sulpho-5-toluate*. The corresponding *barium*, *barium hydrogen*, and *silver* salts are described. By the action of phosphorus pentachloride on the potassium salt, a mixture of two *chlorides* is obtained, which melt at 133° and 93°; it is probable that the compound of higher m. p. is the symmetrical chloride,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me} \begin{smallmatrix} \text{COCl} \\ \text{SO}_2\text{Cl} \end{smallmatrix}$ , whilst the other is the unsymmetrical chloride,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me} \begin{smallmatrix} \text{COCl} \\ \text{SO}_2 \end{smallmatrix} \text{O}$ .

(2) *Potassium 6-nitro-4-sulpho-3-toluate*. The *potassium hydrogen* and *silver* salts are also described. The *acid* crystallises in prismatic plates. The *chloride*, m. p. 90° (corr.), when treated with concentrated ammonia, yields a *compound*, m. p. 274°, which is probably the diamide.

(3) *Potassium dihydrogen 6-nitro-4-sulphoisophthalate*,



The *acid chloride* is obtained in two forms, one, m. p. 147°, crystallising in needles, and the other, an oily liquid; when treated with ammonia, the former gives a *compound*, m. p. 277°, and the latter a *compound*, crystallising in coarse needles. E. G.

**Methyl Salicylate. II. Solubility in Water at 30°.** HARRY D. GIBBS (*Philippine J. Sci.*, 1908, 4, 3, 357—359. Compare *Abstr.*, 1908, ii, 906).—The solubilities of methyl salicylate at 30° in water and N/10 sulphuric acid are shown to be 0.014 and 0.077 gram in 100 grams of solvent respectively. Slight improvements are described in the colorimetric method for determining methyl salicylate (*loc. cit.*). P. H.

**Preparation of o-Alkylthiolbenzoic Acids and their Alkyl Esters.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 203882).—*Methyl o-methylthiolbenzoic acid*,  $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$ , colourless needles, m. p. 66—67°, obtained by adding methyl sulphate to thiosalicylic acid dissolved in aqueous sodium hydroxide, is hydrolysed into *o-methylthiolbenzoic acid*, m. p. 168—170°, this acid being also produced from thiosalicylic acid and sodium methyl sulphate in aqueous sodium hydroxide.

*Ethyl o-ethylthiolbenzoate*,  $\text{SEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ , crystals, m. p. 27—28°, b. p. 152—153°/10 mm., is obtained by treating sodium thiosalicylate with ethyl sulphate; the use of sodium ethyl sulphate in this reaction leads to *o-ethylthiolbenzoic acid*, yellow crystals, m. p. 134—135°.

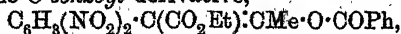
G. T. M.

**Preparation of Alkylthiosalicylic [*o*-Alkylthiolbenzoic] Acids.** FARBERWERKE FORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 203388).—The *o*-alkylthiolbenzoic acids can be produced in one operation from the *o*-aminobenzoic acids by diazotising the latter, neutralising the diazo-solution, and then treating with sodium sulphide and sodium methyl sulphate, gradually heating to 60° or 70°. *o*-Methylthiolbenzoic and ethylthiolbenzoic acids, m. p. 168—169° and 134—135° respectively, were obtained in this way. G. T. M.

**Ethyl  $\alpha$ -Dinitrophenylacetoacetate and Related Compounds.** I. WALTHER BORSCHKE (*Ber.*, 1909, 42, 601—612. Compare Heckmann, *Abstr.*, 1884, 178).—A 75% yield of ethyl  $\alpha$ :2:4-dinitrophenylacetoacetate can be obtained by heating an ethereal solution of chloro-(or bromo)-2:4-dinitrobenzene with a suspension of ethyl sodio-acetoacetate in ether for one hour on the water-bath. The corresponding *methyl* ester,  $C_6H_3(NO_2)_2 \cdot CHAc \cdot CO_2Me$ , crystallises from methyl alcohol in compact, yellow needles, m. p. 114°, and is not so readily soluble as the ethyl ester. The ester forms a stable sodium derivative when its ethereal solution is treated with sodium or sodium ethoxide; but it has not been found possible to replace the sodium by alkyl groups.  $\alpha$ -Alkylated acetoacetic esters do not condense with chloro-2:4-dinitrobenzene.

Dry ammonia reacts with an ethereal solution of the ester, yielding acetamide and ethyl 2:4-dinitrophenylacetate. Phenylhydrazine reacts in a similar manner, yielding ethyl 2:4-dinitrophenylacetate and *s*-acetylphenylhydrazine; with a hot ethereal or alcoholic solution of aniline, 2:4-dinitrophenylacetanilide,  $C_6H_3(NO_2)_2 \cdot CH_2 \cdot CO \cdot NHPh$ , m. p. 181°, is formed.

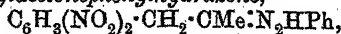
Benzoyl chloride reacts with the sodium derivative of the dinitro-ester, yielding the *O*-benzoyl derivative,



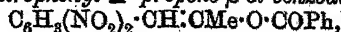
which crystallises from boiling alcohol in rhombic, yellow plates, m. p. 142—143°. When hydrolysed it yields benzoic acid and dinitrophenylacetone. It has not been found possible to transform this *O*-benzoyl into an isomeric *C*-benzoyl derivative.

2:4-Dinitrophenylacetone,  $C_6H_3(NO_2)_2 \cdot CH_2 \cdot CO \cdot CH_3$ , is readily obtained by hydrolysing the original ester with concentrated sulphuric acid, and crystallises from dilute alcohol in brilliant, pale yellow needles, m. p. 75°. The ketone dissolves in dilute alkali hydroxides, yielding blood-red solutions, from which the ketone cannot be recovered. It does not react with aniline even in the presence of formic acid, and with an alcoholic solution of *p*-nitrosodimethylaniline in the presence of sodium hydrogen carbonate yields a small amount of a dark green, crystalline compound, probably the *p*-dimethyl-aminoanil of 2:4-dinitrobenzaldehyde (*Abstr.*, 1902, i, 682).

2:4-Dinitrophenylacetonephenylhydrazone,

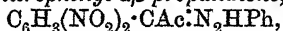


crystallises from hot alcohol in orange-red needles, m. p. 124—125°. The ketone reacts with benzoyl chloride in the presence of pyridine, yielding  $\alpha$ :2:4-dinitrophenyl- $\Delta^{\alpha}$ -propene- $\beta$ -ol benzoate,



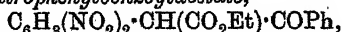
which crystallises from dilute alcohol in pale yellow needles, m. p. 90°.

An alcoholic solution of the ketone reacts with a solution of diazobenzene chloride and sodium acetate, yielding the *α*-phenylhydrazone of *α*-2 : 4-dinitrophenyl-*αβ*-propandione,

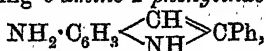


which crystallises from a mixture of alcohol and ethyl acetate in brilliant, orange-red needles, m. p. 201–202° (decomp.). With phenylhydrazone it yields the *bisphenylhydrazone*,  $\text{C}_{21}\text{H}_{18}\text{O}_7\text{N}_6$ , in the form of glistening, black needles, which decompose at 206°. Sodium hydroxide produces a black coloration with an alcoholic solution of the monohydrazone, but this gradually changes to a pale red colour, and the addition of water precipitates a compound,  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}_3$ , which crystallises from a mixture of chloroform and alcohol in pale green, glistening prisms, m. p. 183–184°. This compound is probably 6-nitro-3-acetyl-1-phenylisindazole,  $\text{NO}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{C}(\text{Ac}) \cdot \text{NPh} \cdot \text{N}$  (compare Meyer, Abstr., 1889, 516).

*Ethyl α*-2 : 4-dinitrophenylbenzoylacetate,



is obtained by the action of an alcoholic solution of bromo-2 : 4-dinitrobenzene (1 mol.) on ethyl sodiobenzoylacetate (2 mols.). It forms a yellow oil, and when hydrolysed with concentrated sulphuric acid yields *ω*-2 : 4-dinitrophenylacetophenone,  $\text{C}_6\text{H}_5(\text{NO}_2)_2 \cdot \text{CH}_2 \cdot \text{COPh}$ , which crystallises from a mixture of chloroform and alcohol in slender, colourless needles, m. p. 136–137°. The ketone reacts with stannous chloride solution, yielding 6-amino-2-phenylindole,

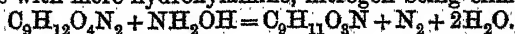


m. p. 240°. The base readily turns dark-coloured on exposure to the air; the *hydrochloride* forms colourless plates, which turn green on exposure to the air. J. J. S.

**Action of Free Hydroxylamine on Lactones.** LUIGI FRANCESCONI and GUIDO CUSMANO (*Gazzetta*, 1909, 39, i, 189–202).—

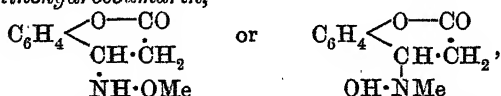
Whilst santonin reacts with 3 mols. of hydroxylamine, one of which unites with the lactone group, desmotroposantonin, which contains the same lactone grouping but no ethylenic linkings, is not attacked by hydroxylamine (compare Abstr., 1908, i, 272). Phthalide is indifferent towards hydroxylamine, whilst coumarin, which contains a double linking in the *β*-position with respect to the carbonyl, takes up 2 mols. of the base. The reaction with coumarin has been studied in detail.

Although Tiemann found (Abstr., 1886, 880) that coumarin did not react with hydroxylamine, the combination readily takes place if a methyl-alcoholic solution of the free base is used and the reacting substances are allowed to remain together for six days. The product is a mixture of *dihydroxylaminohydrocoumarin*,  $\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2$ , white crystals, m. p. 130–131°, and *aminohydrocoumaric* [*aminomelilotic*] acid,  $\text{C}_9\text{H}_{11}\text{O}_5\text{N}$ , m. p. 208°. Low temperature and high concentration favour the formation of the former compound, which at higher temperatures reacts with more hydroxylamine, nitrogen being eliminated :



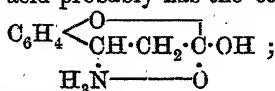
Dihydroxylaminohydrocoumarin dissolves slowly in water to a neutral solution, reduces Fehling's solution, and gives an intense reddish-violet coloration with ferric chloride. It probably contains the lactone ring, and has the constitution  $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH(NH \cdot OH) \cdot CH_2 \end{smallmatrix} \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ C(OH) \cdot NH \cdot OH \end{smallmatrix}$ . It is readily hydrolysed by dilute acids. Acetone forms with it a condensation product,  $C_{12}H_{13}O_3$ , crystallising from alcohol in transparent, rectangular tablets. This product does not reduce Fehling's solution until after hydrolysis.

On attempting to methylate with methyl sulphate, the alkali causes the removal of hydroxylamine from the carbonyl group, and *methylhydroxylaminohydrocoumarin*,



is obtained in large, clear prisms, m. p. 167–168°. The methyl derivative does not reduce Fehling's solution or give a coloration with ferric chloride.

Aminohydrocoumaric acid probably has the constitution



it does not reduce Fehling's solution.

C. H. D.

**Preparation of Substituted o-Carboxy phenylthioglycollic Acids.** FARBERKE VORM. MEISTER, LUCIUS, BRÜNING (D.R.-P., 202243).—The homologues of anthranilic acid, when diazotised and treated successively with a metallic sulphide and sodium chloroacetate, are converted into the corresponding o-carboxyphenylthioglycollic acids in one operation.

6-Carboxy-3-methylphenylthiolacetic acid (annexed formula) is thus produced from homoanthranilic acid. G. T. M.

**Exception to the General Method for Preparation of Aldehydes by means of Glycidic Acids.** RENÉ POINTET (*Compt. rend.*, 1909, 148, 417–419).—The following substituted glycidic acids, prepared by condensing ethyl chloroacetate with ketones of the type  $R \cdot CO \cdot R'$ , do not lose carbon dioxide when heated, and are therefore not available for the preparation of the corresponding aldehydes of the type  $CHRR' \cdot CHO$  by Darzen's method (Abstr., 1905, i, 117).

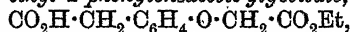
*Diphenylglycidic acid*,  $O \begin{smallmatrix} CPh_2 \\ | \\ CH \cdot CO_2H \end{smallmatrix}$ , m. p. 146°. The ethyl ester has m. p. 47° and b. p. 202–204°/12 mm.

*Phenyl-p-tolylglycidic acid*,  $O \begin{smallmatrix} CPh \cdot C_6H_4Me \\ | \\ CH \cdot CO_2H \end{smallmatrix}$ , m. p. 134°. The ethyl ester has b. p. 225°/18 mm.

*Phenyl-p-anisylglycidic acid*,  $O \begin{smallmatrix} CPh \cdot C_6H_4 \cdot OMe \\ | \\ CH \cdot CO_2H \end{smallmatrix}$ , m. p. 110°. The ethyl ester, has b. p. 240°/20 mm.

When heated, this acid loses carbon monoxide and forms *phenyl-p-anisylacetic acid*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{CO}_2\text{H}$ , m. p.  $100^\circ$ . W. O. W.

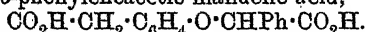
**Attempts to Synthesise Chromenol and its Derivatives.** S. CZAPLICKI, STANISLAUS VON KOSTANECKI, and VICTOR LAMPE (*Ber.*, 1909, 42, 827—838).—Since the direct addition of hydrogen cyanide to salicylaldehyde methyl ether does not give satisfactory results, to prepare *o*-hydroxyphenylacetic acid, the sodium hydrogen sulphite compound of the aldehyde is converted into *o*-methoxymandelonitrile,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CN}$ , and this is heated with eight times its weight of hydrogen iodide. If a smaller proportion is taken, *o*-methoxyphenylacetic acid, m. p.  $124^\circ$ ; described by Pschorr (*Abstr.*, 1900, i, 232), is obtained. The hydroxyphenylacetic acid so obtained forms colourless, glistening prisms, m. p.  $147^\circ$ ; the lactone, *isocoumaranone*, has m. p.  $28 \cdot 5^\circ$ . It reacts with ethylbromoacetic acid in presence of sodium, forming *ethyl 2-phenyleneacetic-glycollate*,



which was converted directly into *o*-phenyleneacetic-glycollic acid by heating with alcoholic potassium hydroxide. This forms colourless needles, m. p.  $158$ — $159^\circ$ , and shows no coloration with ferric chloride; the *diethyl* ester separates in colourless needles, m. p.  $48$ — $49^\circ$ . *p*- and *m*-Hydroxyphenylacetic acids may be prepared in a similar manner, but the yield is much less satisfactory.

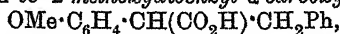
*p*-Methoxymandelonitrile, m. p.  $63^\circ$  (Tiemann and Köhler, *Abstr.*, 1882, 57), is obtained by the action of potassium cyanide on the sodium hydrogen sulphite compound of anisaldehyde, and is converted into *p*-hydroxyphenylacetic acid when boiled with hydriodic acid. *m*-Methoxymandelonitrile is obtained as a yellow oil from *m*-methoxybenzaldehyde in a similar manner, and is converted by hydrogen iodide into *m*-hydroxyphenylacetic acid, m. p.  $129^\circ$  (Salkowski, *Abstr.*, 1884, 1176).

The lactone of *o*-hydroxyphenylacetic acid and ethyl  $\alpha$ -bromophenylacetate interact in presence of sodium in alcoholic solution, forming the *ethyl* ester of *o*-phenyleneacetic-mandelic acid,

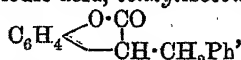


The acid is obtained as a thick oil, which crystallises in short, wide needles, m. p.  $178^\circ$ . The *diethyl* ester forms short, wide needles, m. p.  $61^\circ$ .

*2-Methoxystilbene- $\alpha$ -carboxylic acid*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CO}_2\text{H}) \cdot \text{CHPh}$ , is obtained in colourless, short needles, m. p.  $145$ — $146^\circ$ . It is reduced by sodium amalgam to *2-methoxydibenzyl- $\alpha$ -carboxylic acid*,



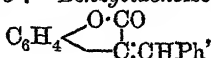
which separates in thick prisms united in masses, m. p.  $93$ — $94^\circ$ . When heated with hydriodic acid, *benzylisocoumaranone*,



is obtained as an oil, which crystallises from alcohol in colourless plates, m. p.  $61^\circ$ . This lactone is converted into *2-hydroxydibenzyl- $\alpha$ -carboxylic acid* when heated with alcoholic potassium hydroxide, but this passes back into the lactone when recrystallised from water.

2:3':4'-Trimethoxystilbene- $\alpha$ -carboxylic acid, prepared by the interaction of veratraldehyde on 2-methoxyphenylacetic acid, crystallises in colourless needles, m. p. 185—186°. 2:3':4'-Trimethoxydibenzyl- $\alpha$ -carboxylic acid forms granular crystals, m. p. 125—126°.

2-Hydroxystilbene- $\alpha$ -carboxylic acid, prepared by the interaction of  $\alpha$ -hydroxyphenylacetic acid and benzaldehyde, crystallises in long, colourless plates, m. p. 155°. Benzylidenisocoumaranone,



formed at the same time as the above, separates in yellow prisms or concentrically-grouped needles. The crystals are coloured orange by concentrated sulphuric acid.

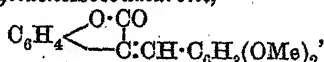
Benzylidenisocoumaranone is the chromogen of a new class of dyes which contain the same complex chromophore ( $\text{CO} \cdot \text{C} \cdot \text{C}$ ) as the oxindogenides,  $\begin{array}{c} \text{O} \cdot \text{C} \cdot \text{CH} \\ \diagdown \text{CO} \end{array}$ , and are therefore termed isooxindogenides.

The three isomeric methoxy-2-hydroxystilbene- $\alpha$ -carboxylic acids have been prepared in a similar manner. They all yield sodium salts sparingly soluble in cold sodium hydroxide, and are converted into the corresponding lactones when melted.

The 2'-methoxy-compound crystallises in needles from benzene or plates from dilute alcohol, m. p. 152°; the 3'-methoxy-derivative forms thick crystals, m. p. 148°; the 4'-methoxy-acid yields broad needles, m. p. 140°.

2'-Methoxybenzylidenisocoumaranone forms broad, prismatic, yellow needles, m. p. 126—127°; the 3'-isomeride forms yellow prisms, m. p. 118—119°; the 4'-lactone separates in yellow needles, m. p. 132°.

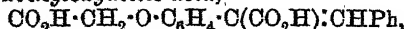
3':4'-Dimethoxybenzylidenisocoumaranone,



forms orange-yellow, prismatic needles, m. p. 99—100°.

2-Hydroxy-3':4'-dimethoxystilbene- $\alpha$ -carboxylic acid, prepared by hydrolysis of the above lactone, crystallises in needles, m. p. 187°.

$\alpha$ -Carboxy-2-stilbenyloxyacetic acid,

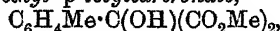


formed by the interaction of hydroxystilbenecarboxylic acid and ethyl bromoacetate, crystallises in plates, m. p. 204—205°.  $\alpha$ -Carboxy-2-dibenzyl oxyacetic acid,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2\text{Ph}$ , separates in rosettes of colourless needles, m. p. 165°. It is obtained either by reduction of the foregoing compound or by the interaction of ethyl-bromoacetate or 2-hydroxydibenzyl- $\alpha$ -carboxylic acid. E. F. A.

Condensation of Mesoxalic Esters with Aromatic Hydrocarbons. ALFRED GUYOT and G. ESTEVA (*Compt. rend.*, 1909, 148, 564—566. Compare this vol., i, 158).—When a mesoxalic ester is treated with an aromatic hydrocarbon in presence of concentrated sulphuric acid, condensation occurs with formation of a substituted tartronic ester of the type  $\text{OH} \cdot \text{CPh}(\text{CO}_2\text{R})_2$ . A portion of this ester undergoes condensation with a second molecule of the hydrocarbon,

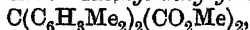
giving a substituted malonic ester of the type  $\text{CPh}_2(\text{CO}_2\text{R})_2$ . The two esters are separated by distillation in a vacuum.

The following compounds have been prepared in this way: *Methyl phenyltartronate*,  $\text{OH}\cdot\text{CPh}(\text{CO}_2\text{Me})_2$ , silky needles, m. p.  $67^\circ$ , b. p.  $165^\circ/11$  mm. The *ethyl* ester occurs as a crystalline mass, m. p.  $28^\circ$ , b. p.  $170^\circ/10$  mm. *Methyl p-tolyltartronate*,



m. p.  $72^\circ$ , b. p.  $175^\circ/11$  mm. The *ethyl* ester forms prisms, m. p.  $41^\circ$ , b. p.  $180^\circ/9$  mm. *Methyl ditolylmalonate*,  $\text{C}(\text{C}_6\text{H}_4\text{Me})_2(\text{CO}_2\text{Me})_2$ , needles, m. p.  $126.5^\circ$ . The *ethyl* ester forms prisms, m. p.  $93.5^\circ$ .

*Methyl o-xyllyltartronate*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{Me})_2$ , needles, m. p.  $94.5^\circ$ , b. p.  $185^\circ/11$  mm. The *ethyl* ester forms a crystalline mass, m. p.  $35^\circ$ , b. p.  $193^\circ/13$  mm. *Methyl dixyllylmalonate*,



m. p.  $135^\circ$ . The *ethyl* ester forms prisms, m. p.  $67^\circ$ . *Ethyl phenyltolylmalonate*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CPh}(\text{CO}_2\text{Et})_2$ , has m. p.  $55.5^\circ$ .

These compounds are also obtained when ethyl oximinomalonate is substituted for ethyl mesoxalate in the above preparation; the yields, however, are poor. W. O. W.

**Compounds from Lichens. XVII. Substances Present in Lobulated Lichens (Peltigeraceæ).** WILHELM ZOFF (*Annalen*, 1909, 364, 273—313. Compare Abstr., 1907, i, 218).—Twelve members of the family *Peltigera* have been investigated, and a hitherto unknown derivative of orcinol, named peltigerin, has been isolated to the extent of 2 to 3% from eight of them, namely, *P. aphthosa*, *P. malacea*, *P. horizontalis*, *P. venosa*, *P. polydactyla*, *P. scabrosa*, *P. propagulisfera*, and *P. lepidophora*. Peltigerin is not present in *P. prætextata*, *P. canina*, *P. rufescens*, *P. spuria*, *Nephroma arcticum*, *N. antarcticum*, *N. resupinatum*, *N. lævigatum*, *N. parile*, *Solorina crocea* or *S. saccata*.

*Peltigerin*,  $\text{C}_{21}\text{H}_{20}\text{O}_8$  or  $\text{C}_{16}\text{H}_{16}\text{O}_8$ , crystallises from acetone or ether in thin, colourless leaflets with a silvery lustre, and from glacial acetic acid in long, slender, curved needles; it sinters at about  $160^\circ$  and changes into a turbid liquid at  $170$ — $180^\circ$ , which becomes transparent at about  $220^\circ$ . When peltigerin is heated carefully, it yields a sublimate consisting of *peltigeric acid*,  $\text{C}_{10}\text{H}_{12}\text{O}_4$ , and *peltigronic acid*. The former acid crystallises in large, compact plates and prisms, m. p. about  $127^\circ$ ; it is coloured red by calcium hypochlorite and gives a violet coloration with ferric chloride. Peltigronic acid crystallises in rosettes of long needles, m. p.  $144$ — $145^\circ$  (decomp.).

Zeorin has been detected in *P. malacea*, *P. horizontalis*, *P. propagulisfera*, *N. arcticum*, *N. antarcticum*, *N. lævigatum*, and *N. parile*. It is not present in the other representatives of these genera which have been investigated.

*d*-Usnic acid was isolated from *Nephroma arcticum* and *N. antarcticum*.

Mannitol has hitherto been obtained from only two lichens; it has now been separated from *P. malacea*, *P. horizontalis*, *P. aphthosa*, *P. polydactyla*, *P. canina*, *P. rufescens*, *P. spuria*, *P. prætextata*,

*Nephroma resupinatum*, *N. lævigatum*, *N. parile*, *Solorina crocea*, and *S. seccata*.

Acids, namely, one from each, have been isolated from *P. scabrosa*, *P. polydactyla*, *P. venosa*, *P. horizontalis*, and *Solorina seccata*; they become red when treated with calcium hypochlorite, but have not been investigated further, owing to the small quantities obtained.

*Peltigera malacea* contains an acid which crystallises in small, white needles, m. p. 220°.

*P. aphthosa* contains two acids, both of which are turned red by calcium hypochlorite; one crystallises in slender needles, softens at 120°, m. p. 125–130°; the other crystallises in small aggregates of slender needles, sinters at 200°, m. p. about 220°.

In addition to soloric acid (compare Zopf, Abstr., 1895, i, 297), *Solorina crocea* contains an acidic substance, which it is proposed to designate *solorinin*; it crystallises in small, thin, colourless leaflets, begins to decompose at about 170°, and forms a reddish-brown liquid at 230°.

*Peltigera canina* contains a neutral substance, *caninin*, crystallising in colourless, rhombic plates.

Two indifferent substances have been isolated from *P. polydactyla*, namely, *polydactylin*, crystallising in silky, white needles, m. p. about 178–180°, and *peltidactylin*, which crystallises in glistening, colourless, rectangular plates, m. p. about 237–240°.

Nephrin was detected in *Nephroma arcticum* and *N. lævigatum*, but not in *N. resupinatum* or *N. antarcticum* (compare Hesse, Abstr., 1898, i, 679).

W. H. G.

The Oxidation of Organic Compounds by means of the Compounds of Nitric Acid with Aldehydes or Ketones. ALEXIS A. SHUKOFF (D.R.-P. 206695).—The aldehydes and ketones readily form nitrates when added to concentrated nitric acid, the product usually crystallising out. *Benzaldehyde nitrate*, m. p. -1°, is obtained by adding the aldehyde to fuming nitric acid and cooling to -10°. *Camphor nitrate*, m. p. 180°, produced by adding 152 parts of camphor to 70 parts of fuming nitric acid, separates on cooling with ice. These substances are convenient oxidising agents for organic compounds which may be dissolved in these very fusible nitrates and left to oxidise at the ordinary temperature. Anthracene dissolves in benzaldehyde nitrate on gently warming, and anthraquinone separates forthwith. Borneol and isoborneol are similarly oxidised to camphor.

G. T. M.

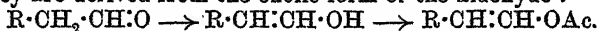
Condensation of Aminohydroxy-acids with Aromatic Aldehydes. ERNESTO PUXEDDU (*Gazzetta*, 1909, 39, i, 121–131. Compare Abstr., 1908, i, 286).—In continuation of former work on the influence of substituents on the condensation of aminohydroxy-acids with aldehydes, it has been found that *o*- and *p*-nitrobenzaldehyde readily condense with 5-amino-*o*- or -*m*-cresotic acid. Unlike salicylaldehyde, *p*-hydroxybenzaldehyde does not condense with either acid. Anisaldehyde, *p*-tolualdehyde, and catechualdehyde are also without action, whilst vanillaldehyde condenses with 5-amino-*o*-cresotic acid,

although slowly, but not with its meta-isomeride. In the latter case, the methyl group is in the ortho-position relatively to the nitrogen atom.

The products are coloured, crystalline substances, insoluble in water and in most organic solvents, except alcohol and acetic acid. They are acid in character. Their constitution is under investigation.

The compound from 5-amino-*m*-cresotic acid and *p*-nitrobenzaldehyde forms a *hydrochloride*, m. p. 96°. C. H. D.

**Constituents of Ethereal Oils: Further Decomposition of Eksantalal; Enolisation of Aldehydes by Conversion into the Corresponding Unsaturated Esters; enol-Phenylacetaldehyde-monoacetate.** FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 584—591).—In the work on essential oils, it has been frequently noticed that although secondary alcohols give good yields of ketones when oxidised with an acetic acid solution of chromic anhydride, only poor yields of aldehydes can be obtained from primary alcohols under similar conditions, appreciable amounts of less volatile products being formed at the same time. This is now shown to be due to the enolising action of the acetic acid and the formation of an acetate of the unsaturated alcohol. These acetates are termed monoacetates in order to distinguish between them and the diacyl derivatives to which aldehydes give rise; the prefix enol is also used in order to indicate that they are derived from the enolic form of the aldehyde:



It is only aldehydes which contain hydrogen attached to the  $\alpha$ -carbon atom which can react in this manner.

enol-Phenylacetaldehyde monoacetate (*phenylvinyl acetate*),  
 $CHPh : CH \cdot OAc$ ,

is readily formed when the aldehyde is boiled for an hour with twice its weight of acetic anhydride; it has b. p. 119—121°/10 mm.,  $D^{20}_D$  1.065,  $n_D$  1.5483. When reduced it yields phenylethyl alcohol and ethyl alcohol, and when oxidised with ozone the products are benzaldehyde and benzoic acid. Hydrolysis with dilute mineral acids at 100—110° yields phenylacetaldehyde and acetic acid. Phenylacetaldehyde has b. p. 85—86°/10 mm.,  $D^{20}_D$  1.0252, and  $n_D$  1.53191. Heptaldehyde, citral, citronellal, and various other aldehydes react in a similar manner.

The formation of these esters of the enolised aldehydes affords the basis of a simple method by means of which the aldehyde group CHO can be removed and an aldehyde or ketone containing one less carbon atom obtained.

The readiness with which aldehydes form acetates must be borne in mind when estimating the amount of alcohol present in an essential oil.

Tricyclic enol-eksantalal monoacetate,  $C_{10}H_{14} : CH \cdot OAc$ , has b. p. 132—135°/10 mm.,  $D^{20}_D$  1.023, and  $n_D$  1.4881, and is laevorotatory. It is usually accompanied by a small amount of a diacetate,  $C_{15}H_{22}O_4$ , which has a higher b. p.

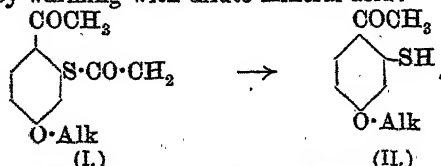
When reduced, the monoacetate yields eksantalol,  $C_{11}H_{18}O$ , and when oxidised with ozone in benzene solution yields tricyclic nor-eksantalone,  $C_{10}H_{14}O$ , which has b. p. 101—102°/10 mm.,  $D^{20}_D$  0.988.

and  $n_D$  1.485. It yields a *semicarbazone*,  $C_{10}H_{14}:N \cdot NH \cdot CO \cdot NH_2$ , m. p. 216°, and an *oxime*,  $C_{10}H_{14}:N \cdot OH$ , b. p. 142—144°/10 mm.

The behaviour of *eksantalal* indicates that it contains a hydrogen atom attached to the carbon atom which is in the  $\alpha$ -position with respect to the aldehyde group. J. J. S.

**Constitution of Dichloropiperonal.** GEORGE BARGER (*Ber.*, 1909, 42, 763—765. Compare *Trans.*, 1908, 93, 563, 735).—Polemical. A reply to Pauly (this vol., i, 165). W. R.

**Preparation of 5-Alkyloxy-2-acetylphenyl Mercaptan.** FARBERKE VORN. MEISTER, LUCIUS & BRÜNING (D.R.-P. 202632).—When treated with acetyl chloride in the presence of aluminium chloride, the 3-alkoxyphenyl mercaptans give rise to diacetyl derivatives (I), from which the alkyloxyacetylphenyl mercaptans (II) are produced by warming with dilute mineral acid:



5-Methoxy-2-acetylphenyl mercaptan, colourless plates, m. p. 94—96°, and 5-ethoxy-2-acetylphenyl mercaptan, colourless crystals, m. p. 68°, which are thus produced, yield sulphur colouring matters on oxidation. G. T. M.

**Organic Syntheses by means of Sunlight.** EMMANUEL PATERNÒ (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 104—105\*).—A solution of benzophenone in amylene, exposed to sunlight, deposits in a few days large crystals of a *compound*, m. p. 109°, which may be converted into a hydrocarbon containing 18 atoms of carbon; it therefore probably has the amylene chain attached to the carbonyl carbon, the oxygen forming a bridge. Oxidation regenerates benzophenone. Acetophenone and amylene yield a liquid *compound*, boiling at 235—237°. The *compound* from benzaldehyde and amylene boils at 229—231°.

Octane and decane react with benzophenone in sunlight, being partly converted into benzopinacolone and unsaturated hydrocarbons, the latter then reacting with benzophenone to form compounds analogous to that from amylene. Some of these compounds are found by analysis and cryoscopic measurements to be formed from 1 mol. of benzophenone and 1 mol. of unsaturated hydrocarbon, but their properties are similar to those of the resins, which may also have a simple constitution.

Benzene does not react with benzophenone, whilst its homologues undergo complex reactions. With ethylbenzene the principal product is a crystalline *compound*, m. p. 88—89°, which has the properties of a tertiary alcohol, and yields a *hydrocarbon*, m. p. 124—126°, and a resin.

Certain alcohols, ethers, and esters react in similar manner to the hydrocarbons. C. H. D.

\* and *Gazzetta*, 1909, 31, i, 237—250.

**Crystallography of Nitrodesmotroposantonin and  $\beta$ -Naphthyl Propyl Ketone.** ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 129—132).—Nitrodesmotroposantonin (Bargellini and Daconto, *Abstr.*, 1908, i, 819) forms rhombic crystals,  $a:b:c = 0.4133:1:2.2646$ . It is dextrorotatory in solution.

$\beta$ -Naphthyl propyl ketone forms triclinic crystals, sometimes several centimetres in length,  $a:b:c = 0.6774:1:0.6029$ ,  $\alpha = 94^\circ 31'$ ,  $\beta = 140^\circ 3.5'$ ,  $\gamma = 90^\circ 27'$ . C. H. D.

**9-Formylfluorene.** I. WILHELM WISLICENUS and MARTIN WALDMÜLLER (*Ber.*, 1909, 42, 785—789. Compare Wislicenus and Densch, *Abstr.*, 1902, i, 291).—9-Formylfluorene, obtained by the condensation of fluorene and ethyl formate, using dry potassium ethoxide as the condensing agent, exists in two tautomeric forms.

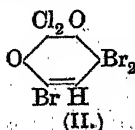
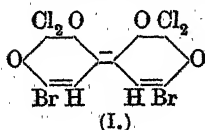
$\alpha$ -Formylfluorene,  $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C}:\text{CH}\cdot\text{OH}$ , is a yellow, viscid oil, b. p. 196—197°/14 mm., 193—193.5°/12 mm., which slowly changes into a solid, transparent, yellow, resinous mass. Mol.-wt. determinations of the latter substance show that it is *bimolecular* formylfluorene,  $(\text{C}_{14}\text{H}_{10}\text{O})_2$ ; it yields the unimolecular variety when distilled under reduced pressure.  $\alpha$ -Formylfluorene, when treated with phenylcarbimide, yields the *additive* product,  $\text{C}_{18}\text{H}_8:\text{CH}\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$ , which crystallises in colourless needles, m. p. 145—146°; the *benzoate*,  $\text{C}_{18}\text{H}_8:\text{CH}\cdot\text{OBz}$ , forms small, slender, colourless needles, m. p. 153—159°; the *acetate*,  $\text{C}_{18}\text{H}_8:\text{CH}\cdot\text{OAc}$ , crystallises in small, colourless plates, m. p. 132—134°.

$\beta$ -Formylfluorene,  $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CH}\cdot\text{CHO}$ , obtained by treating a solution of the  $\alpha$ -modification in aqueous alkali with dilute sulphuric acid, crystallises in colourless, glistening leaflets; it turns yellow and sinters at 70°, and is completely converted into the  $\alpha$ -form at about 90°. The *phenylhydrazone*,  $\text{C}_{20}\text{H}_{16}\text{N}_2$ , crystallises in almost colourless leaflets, m. p. 126—127°; the *anilino*-derivative,  $\text{C}_{20}\text{H}_{15}\text{N}$ , forms small, glistening, yellow needles, m. p. 155°. W. H. G.

**Tribromoresoquinone.** THEODOR ZINCKE and F. SCHWABE (*Ber.*, 1909, 42, 797—802).—The statement of Meyer and Desamari (*Abstr.*, 1908, i, 658) that tribromoresoquinone is a tribromo-*m*-benzoquinone is refuted; it is either a derivative of *p*-dibenzoquinone or *o*-dibenzoquinone, although the latter is very improbable.

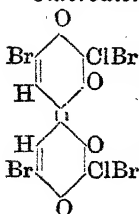
This statement is supported by (1) mol.-wt. determinations; (2) reduction of the substance to tetrabromodiresorcinol; (3) conversion of the reduction product by bromine and water at the ordinary temperature into tribromoresoquinone, and by chlorine under similar conditions into a chlorodibromoresoquinone.

Dichlorotribromoresorcinol, when heated, loses bromine and passes into dichlorobromoresoquinone (compare Benedikt, *Abstr.*, 1879, 55, 464, 717). It is very probable that the latter substance is analogous with tribromoresoquinone, and has the formula (I),



whilst the substance from which it is prepared is a ketochloride having the constitution (II).

*Chlorodibromoresoquinone*, obtained by the action of chlorine on a solution of tetrabromodiresorcinol in dilute acetic acid, crystallises in nodules of small, yellow needles, m. p.  $212^{\circ}$  (decomp.). It is reduced to *dichlorodibromodiresorcinol*,  $C_{12}H_6Cl_2Br_2O_4$ , crystallising in long, slender needles, m. p.  $271^{\circ}$ ; the same substance is apparently produced by the reduction of dichlorobromoresoquinone.



W. H. G.

**Preparation of Anthraquinone- $\alpha\beta$ -sulphonic Acids.** R. WEDEKIND & Co. (D.R.-P. 202398).—The  $\beta$ -anthraquinone mono- and di-sulphonic acids undergo sulphonation with fuming sulphuric acid in the presence of mercury or mercuric salts, and give rise to new polysulphonic acids containing sulphonic groups in  $\alpha$ -positions. Anthraquinone-3-sulphonic acid sulphonated at  $160^{\circ}$  with fuming acid (40%  $SO_3$ ), and a small amount of mercuric sulphate furnishes chiefly anthraquinone-1:6- and -1:7-disulphonic acids. These acids are also obtained by starting with anthraquinone itself and sulphonating as before in the presence of mercuric sulphate, employed in a coarse, granular form.

G. T. M.

**Preparation of Halogenated Anthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 205913. Compare following Abstract).—The replacement of the sulphonic group by halogen in the anthraquinonedisulphonic acids may be effected in two stages by employing moderate amounts of halogenating agent. *Potassium 1-chloroanthraquinone-5-sulphonate*, pale yellow needles, is obtained by treating sodium anthraquinonedisulphonate with sodium chlorate and hydrochloric acid and salting out the product with potassium chloride so soon as appreciable amounts of the original disulphonate are no longer apparent. *Potassium 1-bromoanthraquinone-5-sulphonate*, yellow needles, is produced in a similar manner by employing bromine instead of chlorate and hydrochloric acid.

Similar results are obtained with anthraquinone-1:8- and -2:7-disulphonic acids, the sulphonic groups being replaced by chlorine in two stages.

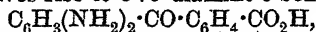
G. T. M.

**Replacement of Halogen by Hydroxyl in Substituted Anthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 203083).—When the halogenated anthraquinones are heated with fuming sulphuric acid, either with or without boric acid, the halogen atoms are more or less replaced by hydroxyl. 1:4-Dichloroanthraquinone and 4-chloro-1-hydroxyanthraquinone give rise to quinizarin (1:4-dihydroxyanthraquinone), and 2:4-dibromo-1-aminoanthraquinone furnishes 2-bromo-4-amino-1-hydroxyanthraquinone, m. p.  $243^{\circ}$ .

G. T. M.

[Preparation of Alkylaminoanthraquinone Derivatives.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205096).—Potassium 1:4-diethylaminoanthraquinone-5-sulphonate, blue needles with bronzy lustre, is obtained by heating at 100—120° aqueous ethylamine and the leuco-derivative of potassium quinizarin-5-sulphonate; by using methylamine, the corresponding dimethylaminoanthraquinone-5-sulphonate was produced. G. T. M.

Preparation of Derivatives of 1:3-Diaminoanthraquinone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205036).—*o*-Benzoylbenzoic acid on treatment with concentrated nitric and sulphuric acids furnishes among other products 3:5-dinitro-*o*-benzoylbenzoic acid, which on reduction gives rise to 3:5-diamino-*o*-benzoylbenzoic acid,



this substance having the property of condensing with great readiness to form 1:3-diaminoanthraquinone.

Trinitro-2-*p*-toluoylbenzoic acid, m. p. 217—218.5°, from the nitration of 2-*p*-toluoylbenzoic acid, is reduced by iron and acetic acid to triamino-2-*p*-toluoylbenzoic acid, which on warming with dilute ammonia gives 1:3-(?)-triamino-2-methylanthraquinone, yellowish-red needles, m. p. above 300°.

1:3-Diamino-2-methylanthraquinone, yellowish-red needles, m. p. 273—276°, is obtained by reducing 1:3-dinitro-2-*p*-toluoylbenzoic acid with iron and dilute acetic acid; the intermediate 1:3-diamino-2-*p*-toluoylbenzoic acid having largely condensed during reduction, the remainder is condensed by warming with acetic acid.

1:3-Diamino-2-methoxyanthraquinone, reddish-yellow needles, m. p. 225—230°, is obtained by a similar set of operations from *p*-anisoylbenzoic acid. G. T. M.

[Preparation of Leuco-derivatives of Diaminoanthraquinones from the Corresponding Hydroxylic Compounds.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205149).—The leuco-derivative of quinizarin when heated with alcoholic ammonia (25%) at 100° gives rise to the leuco-derivative of 1:4-diaminoanthraquinone, leaflets with green metallic reflex, m. p. 272° (decomp.). The leuco-derivative of 1:4:5:8-tetrahydroxyanthraquinone, obtained by reducing the tetrahydroxy-compound with alkali hyposulphite, when treated with alcoholic ammonia gives rise to the leuco-derivative of 1:4-diamino-5:8-dihydroxyanthraquinone, needles, decomposing at 284°. Other leuco-derivatives of the hydroxyanthraquinones undergo this change on treatment with ammonia. G. T. M.

Preparation of Arylaminoanthraquinones. FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 201905).—4-Amino-1-*p*-tolyl-amino-8-methoxyanthraquinone, lustrous, coppery leaflets, m. p. 226°, is prepared by heating 4-nitro-1:8-dimethoxyanthraquinone with *p*-toluidine and stannous chloride at 60—90°; its sulphonic acids are wool dyes giving faint shades of blue. G. T. M.

Preparation of 4-Chloro-1-hydroxyanthraquinone. R. WEDEKIND & Co. (D.R.-P. 202770).—4-Chloro-1-hydroxyanthraquinone is

readily obtained by adding simultaneously to 1-hydroxyanthraquinone, suspended in strong sulphuric acid at 110—115°, solutions of potassium chlorate and hydrochloric acid.

G. T. M.

**Preparation of Thiocyanogen Derivatives of Anthraquinone.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206054).—The replacement of the diazonium group by thiocyanogen occurs readily in the benzene and naphthalene series only in the presence of cuprous thiocyanate. In the anthraquinone series this replacement takes place merely on boiling the diazonium thiocyanate with water.

*α*-Thiocyanoanthraquinone,  $\text{ONS} \cdot \text{C}_{14}\text{H}_9\text{O}_2$ , yellow needles, m. p. 231°, was obtained by diazotising *α*-aminoanthraquinone in concentrated sulphuric acid and boiling the aqueous solution of the diazo-salt with potassium thiocyanate. Other thiocyano-derivatives with this group in positions 2 and 1:5 are similarly produced.

G. T. M.

**Preparation of Benzanthrone and its Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 204354. Compare Abstr., 1907, i, 324, 943; 1908, i, 193, 661).—The aminoanthraquinones and their derivatives condense with glycerol and concentrated sulphuric acid to yield benzanthrone derivatives; it has now been found that this condensation can be effectively carried out by using instead of glycerol such of its derivatives as mono- and di-chlorohydrin and acetin (glyceryl acetate).

G. T. M.

**Preparation of Halogen Derivatives of Benzanthrone.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205294).—*β*-Chloro-benzanthrone, dark green powder or yellow needles, is obtained by condensing *β*-chloroanthraquinone with glycerol, aniline sulphate, and concentrated sulphuric acid at 140°. In this condensation acetin may be employed instead of glycerol.

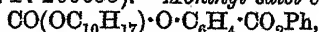
More highly halogenated benzanthrone derivatives can be similarly prepared from dichloro- and dibromo-anthraquinone.

G. T. M.

**Crystallography of the Anhydride of Menthyl Xanthate.** N. SURGUNOFF (*Zeitsch. Kryst. Min.*, 1909, 46, 219—220; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 142—152).—The crystals are hemihedral-rhombic [ $a:b:c = 1.4478:1:2.3533$ ].

L. J. S.

**The Preparation of Mixed Carbonates from Hydroaromatic Alcohols and Ethyl Salicylate.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206055).—*Menthyl salol carbonate*,



colourless crystals, m. p. 57—58, is produced by condensing salol and menthyl chlorocarbonate in benzene containing pyridine; it is also formed by the interaction of salol chlorocarbonate and menthol in the presence of quinoline.

*Menthyl salicylacetol carbonate*,  $\text{CO}(\text{OC}_{10}\text{H}_{17}) \cdot \text{OC}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{COMe}$ , colourless, tasteless crystals, m. p. 87°, is prepared from menthyl chlorocarbonate and acetonyl salicylate,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{CH}_2 \cdot \text{COMe}$ .

*Thymyl salol carbonate* from salol chlorocarbonate and thymol, forms colourless and odourless needles, m. p. 78—79°.

*Santalyl salacetol carbonate*, a yellow, syrupy liquid, is produced from santalol and salacetol chlorocarbonate, the latter reagent being obtained by the interaction of carbonyl chloride and salacetol in the presence of dimethylaniline. The patent refers to several other mixed carbonates of a similar type. G. T. M.

[Preparation of Bornyl Acetate.] OTTO ZEITSCHEL (D.R.-P. 204163).—The existing process for the production of bornyl acetate from pinene is expensive, owing to the large proportion of glacial acetic acid employed. It has now been found that this ester can be produced from its generators, French turpentine and glacial acetic acid, when interacting in molecular proportions at 200° for about five hours. In this way 30—40% of bornyl acetate, 30—40% of limonene, and 10—15% of camphene are obtained. G. T. M.

Preparation of Bornyl and *iso*Bornyl Bromo*iso*valerates. CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 205263 and 205264).—*Bornyl bromoisovalerate*,  
 $\text{CHMe}_2\cdot\text{CHBr}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{17}$ ,

oil, b. p. 163°/10 mm., is obtained by heating in chloroform solution equivalent quantities of borneol and bromo*iso*valeryl chloride or bromide; it may also be obtained from borneol and bromo*iso*valeric anhydride at 100°, bromo*iso*valeric acid and concentrated sulphuric acid at 80°, or from camphene and bromo*iso*valeric acid in the presence of zinc chloride.

*iso*Bornyl bromo*iso*valerate, oil, b. p. 160°/3 mm., is similarly prepared, and can also be produced by mixing *isobornyl iso*valerate with bromine at 100°; a bromine carrier accelerates this action, which takes a similar course with bornyl *iso*valerate. G. T. M.

Crystallography of Two Xanthogenamides (Thio-urethanes). EYGRAF S. FEDOROFF and D. N. ARTEMÉEFF (*Zeitsch. Kryst. Min.*, 1909, 46, 215—218; from *Bull. Soc. Nat. Moscou*, 1906, Nos. 1 and 2, 110—132. Compare Tschugaeff, Abstr., 1902, i, 604).—1-Phenyl-3-*l*-bornyl-2-ethyl-iminoxanthide, monoclinic [ $\alpha : b : c = 0.5785 : 1.0 : 0.5008$ ;  $\beta = 100^\circ 59'$ ]. 1:2-Diphenyl-3-fenchyl-iminoxanthide, rhombic [ $\alpha : b : c = 0.9484 : 1.0 : 0.9512$ ]. L. J. S.

Optically Active Menthones. ERNST BECKMANN (*Ber.*, 1909, 42, 846—850).—*l*-Menthone, obtained from *l*-menthol by oxidation with chromic acid; has  $[\alpha]_D - 28.5^\circ$ ; when inverted with 90% sulphuric acid in the cold, it has  $[\alpha]_D + 28.1^\circ$ . This product is a mixture of *l*-menthone with a highly dextrorotatory *d*-isomenthone. The mixture of oximes from the product can be separated by dissolving in ether and passing in dry hydrogen chloride. A crystalline precipitate, m. p. 132°,  $[\alpha]_D + 35.9^\circ$ , is obtained, whilst the mother liquors yield a compound having m. p. 117—118°,  $[\alpha]_D - 62.6^\circ$ . These are identical with the oxime hydrochlorides of *d*-isomenthone and *l*-menthone. The corresponding oximes have the following constants: *d*-isomenthone-oxime,  $[\alpha]_D + 41^\circ$ , syrup; *l*-menthoneoxime,  $[\alpha]_D - 42.5^\circ$  m. p. 59°.

*d*-isoMenthone gives the same product on inversion as *l*-menthone. *d*-isoMenthone semicarbazone crystallises in colourless needles, m. p. 154°,  $[\alpha]_D + 46.5^\circ$ . *l*-Menthone semicarbazone has m. p. 184°,  $[\alpha]_D - 64^\circ$ . From "inverted" menthone a semicarbazone, m. p. 116°,  $[\alpha]_D + 26.6^\circ$ , has been obtained (compare Barrowcliff, Trans., 1907, 91, 863).

E. F. A.

**Preparation of Camphor.** SCHMITZ & Co. (D.R.-P. 203791).—The metallic derivatives of borneol and isoborneol are readily oxidised to camphor and metallic hydroxide. A current of air passed through a cold toluene solution of sodium isobornyl-oxide or calcium bornyl-oxide leads to the production of camphor and sodium hydroxide or calcium hydroxide respectively. A similar result is obtained by warming together (in xylene) mercuric oxide and sodium isobornyl-oxide.

G. T. M.

[The Interaction of Hydroaromatic Ketones and Magnesium Aryl Halides.] BRUNO SZELINSKI (D.R.-P. 202720).—Carvone and pulegone, when submitted to the Grignard reaction with magnesium aryl halides, furnish the following compounds: *benzyl-dihydrocarvone*, m. p. 69°, b. p. 204–206°/26 mm., *oxime*, m. p. 138°;  *$\alpha$ -naphthylidihydrocarvone*, viscid oil, m. p. 150°, b. p. 230–233°/34 mm., *oxime*, oily; *benzylidihydropulegone*, b. p. 210–215°/35 mm., *oxime*, oily.

These products, when mixed with collodion, wool, or cellulose acetate, give rise to transparent, flexible celluloid, which is more resistant to heat than camphor-celluloid, and has a much higher decomposition point.

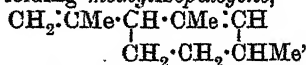
G. T. M.

*iso*Pulegone. ALFRED EBERT (*Chem Zentr.*, 1909, i, 21; from *Zeitsch. Allg. Oesterr. Apoth.-Ver.*, 1908, 545, 561, 573, 589).—When *iso*pulegone,  $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2$ , prepared from citronell-

aldehyde (Tiemann and Schmidt, Abstr., 1897, i, 198), is dissolved in ether and submitted to the action of magnesium methyl iodide,

*methylisopulegyl alcohol*,  $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2$ , is obtained.

It is a pale yellow liquid, having a geranium-like odour, b. p. 93–94°/12 mm.,  $D_{20}^{20} 0.91085$ ,  $[\alpha]_D^{20} 19.54^\circ$ ,  $n_D^{20} 1.46992$ . In cold ethereal solution this substance reacts with phosphorus trichloride, forming *methylisopulegyl chloride*,  $\text{C}_{11}\text{H}_{19}\text{Cl}$ , a colourless liquid, b. p. 92–93°/10 mm., which loses HCl when boiled for three hours with alcohol and potassium acetate, yielding *methylisopulegene*,



a colourless liquid, b. p. 95–97°/12 mm., 182–184°/750 mm.,  $D_{20}^{20} 0.84$ ,  $[\alpha]_D^{20} + 46.27^\circ$ ,  $n_D^{20} 1.4724$ .

*Methylisopulegene* is also obtained by distilling, under ordinary pressure, the crude product of acetylating *methylisopulegyl alcohol*.

I. V. E.

**Preparation of Santalol Ethers.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 202352).—*Santalyl methyl ether*, colourless liquid, b. p. 149—156°/16 mm., was obtained by the following processes: (1) boiling together santalyl chloride and methyl-alcoholic sodium methoxide; (2) adding methyl sulphate to sodium santalol suspended in ether; (3) heating together sodium santalol and methyl iodide in toluene.

*Santalyl ethyl ether*, colourless liquid, b. p. 169—174°/22 mm., was prepared from santalyl bromide and alcoholic sodium ethoxide.

*Santalyl phenyl ether*, viscid oil, b. p. 232°/20 mm., and *santalyl menthyl ether*, colourless syrup, b. p. 201—210°/5 mm., were obtained by heating santalyl chloride in xylene solution with sodium phenoxide and sodium menthoxide respectively. G. T. M.

**Preparation of Santalyl Halides.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 203849).—*Santalyl chloride*, oil, b. p. 162—167°/15 mm., is readily prepared by heating under reduced pressure *santalyl chlorocarbonate*, obtained by the interaction of carbonyl chloride and santalol or sandal oil in the presence of dimethylaniline in benzene solution; it may also be produced by the action of phosphorus pentachloride or thionyl chloride. Santalyl bromide is similarly obtained from phosphorus pentabromide.

G. T. M.

**Preparation of Santalyl Allophanate.** VEREINIGTE CHININ-FABRIKEN ZIMMER & Co. (D.R.-P. 204922).—*Santalyl allophanate*,  $C_{15}H_{23}O \cdot CO \cdot NH \cdot CO \cdot NH_2$ , white needles, m. p. 162°, may be prepared in a variety of ways: (1) Cyanic acid is added to santalol dissolved in light petroleum; (2) santalol is added to a benzene solution of carbamide chloride, either alone or in presence of dimethylaniline; (3) santalol and phenyl carbamate or allophanate are heated under reduced pressure.

G. T. M.

**An Aldehyde from Pinene.** CARL D. HARRIES and HANS VON SPLAWA-NEYMAN (*Ber.*, 1909, 42, 879—880).—By boiling pinene ozonide with water, Harries and Neresheimer (*Abstr.*, 1908, i, 194) were unable to characterise the aldehydic substance formed, but the present authors find that the decomposition proceeds more smoothly in glacial acetic acid solution at 90°. After evaporating the acetic acid in a vacuum at 35°, the residue is fractionated under 12 mm. pressure. The fraction distilling at 115—125° gives with semicarbazide the *disemicarbazone* of *pinonaldehyde*,  $C_{12}H_{22}O_2N_2$ , which crystallises in small, round aggregates, m. p. 214—215°.

J. C. C.

**Preparation of Camphene.** CHEMISCHE FABRIK VORM. SANDOZ (D.R.-P. 204921).—It was already known that the velocity of hydrolysis of pinene hydrochloride by alkali hydroxide is increased by the presence of feebly acidic substances, such as phenols and naphthols. It is now found that this result is effected by neutral compounds, such as sodium or calcium toluene-*p*-sulphonate, sodium naphthalene- $\beta$ -sulphonate, and sodium naphthalene-2 : 7-disulphonate.

G. T. M.

**Elaterin and Some of its Derivatives.** ARMAND BERG (*Compt. rend.*, 1909, 148, 566—568. Compare Abstr., 1898, ii, 447; 1906, i, 596; 1907, i, 146; Pollak, Abstr., 1906, i, 973).—Polemical against Hemmelmayer (Abstr., 1907, i, 230). The author maintains the accuracy of his formula for elaterin,  $C_{28}H_{38}O_7$ , which he has confirmed by determinations of the molecular weight of diacetyelaterin and other derivatives.

Hemmelmayer's "elateridin," obtained in the hydrolysis of elaterin by sulphuric acid, is stated to have the formula  $C_{26}H_{36}O_6$ . The author proposes to call this compound *anhydroelateridin* and to reserve the name elateridin for the substance obtained when the hydrolysis is effected by alcoholic potassium hydroxide. Analysis and molecular-weight determinations by the cryoscopic method show that elateridin has the formula  $C_{26}H_{38}O_7$ .

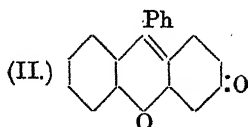
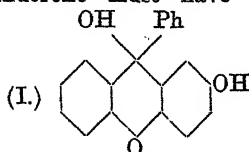
On treatment of elaterin with bromine, a mixture of amorphous bromo-derivatives is obtained; since these cannot be separated by crystallisation, Hemmelmayer's determination of the molecular weight of the product cannot be regarded as establishing his formula for elaterin. W. O. W.

**The Phosphorus Content of Chlorophyll.** JULIUS STOKLASA, VLADIMIR BRDLIK, and ADOLF ERNEST (*Ber. Deut. bot. Ges.*, 1907, 27, 10—20. Compare Abstr., 1908, i, 279).—Polemical against Tsvett (Abstr., 1908, i, 440) and Willstätter (Abstr., 1907, i, 71). Chlorophyll contains phosphorus as glycerophosphoric acid. Tsvett's partial agreement with Willstätter (who denies that chlorophyll contains phosphorus) is not based on experimental results. The authors show by Tsvett's own "chromatographic" method (adsorption of the pigments by calcium carbonate) that phosphorus always accompanies the chlorophyll in adsorption, and that in autumn when the green colour disappears from the leaves, the phosphorus also disappears. G. B.

**Completely Methylated Flavonol Derivatives.** NICOLAI WALLASCHKO (*Ber.*, 1909, 42, 726—728).—In reply to Herzig and Hofmann (this vol., i, 165) the author states that trimethyl- and pentamethyl-quercetin are readily obtained from quercetin, methyl sulphate, and potassium hydroxide under his conditions (Abstr., 1904, i, 760). The ready formation of the pentamethylated derivative necessitates an alteration of Kostanecki and Dreher's generalisation (Abstr., 1893, i, 217), the revised version of which should read: the alkylation of the hydroxyl group ortho to the carbonyl group, whilst not accomplished, or to only slight extent, by an alkyl halide, is readily effected by methyl sulphate and an alkali hydroxide. C. S.

**Constitution of the Fluorescein and Quinolophthalein Dyes.** WALTER KROPP and HERMAN DECKER (*Ber.*, 1909, 42, 578—584).—Kehrmann and Dengler have recently (Abstr., 1908, i, 1002) prepared phenylfluorone, the chromogen of fluorescein, to which they assigned an ortho-quinonoid constitution, and the present authors have endeavoured to prepare the corresponding chromogen of quinolphthalein by the hydrolysis of 2-methoxy-9-phenylxanthonium bromide (compare

Decker and von Fellenberg, Abstr., 1907, i, 1065) and subsequent neutralisation, but they find the only product to be a colourless carbinol base, namely, 2-hydroxy-9-phenylxanthen-9-ol (formula I). There is thus a fundamental difference between the two series of compounds, and the conclusion is drawn that Kehrmann and Dengler's phenylfluorone must have a para-quinonoid structure (II), and



consequently fluorescein must also possess the older para-quinonoid constitution, whilst the ortho-quinonoid formula for the alkali salts of quinolphthalein, which is the only one that explains their colour, cannot be upheld.

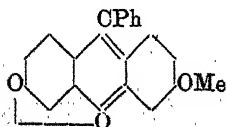
*2-Hydroxy-9-phenylxanthonium bromide*,  $C_6H_4 \begin{matrix} \text{CPh} \cdot \text{C} \cdot \text{CH} : \text{C} \cdot \text{OH} \\ \text{OBr} \cdot \text{C} \cdot \text{CH} : \text{CH} \end{matrix}$ ,

prepared by heating 2-methoxy-9-phenylxanthen-9-ol with hydrobromic acid, crystallises in dark red plates, which darken on warming, and melt and decompose at about  $300^\circ$ . On hydrolysis it yields 2-hydroxy-9-phenylxanthen-9-ol, crystallising in colourless, rhombic prisms, m. p.  $158-160^\circ$  (decomp.). The *chloride*, red rosettes of plates; *iodide*, long, blackish-red plates; *platinichloride*, dark red needles, and *ferrichloride*, dark red crystals, m. p.  $193-194^\circ$  (corr.), are described.

When 3-methoxy-9-phenylxanthonium chloride is heated with hydrochloric acid under pressure, the corresponding hydroxy-compound is formed, which with sodium hydroxide furnishes phenylfluorone. The properties of this compound are not those of a phenolbetaine, which should be soluble in water and not extractable from its solutions by ether or benzene. Moreover, it should (were it a betaine) be at least as strongly coloured as the oxonium salts, but it is only orange-yellow, whilst the corresponding salts are red. It is therefore to be regarded as the chromogen of fuchsone, a conclusion which is confirmed by R. Meyer's observation of the correspondence between the spectrum curves of the fluoresceins and phthaleins.

J. C. C.

**Carboxonium Dyes. II. Strongly Basic, Neutral, Salt-forming, Nitrogen-free Oxonium Compounds and the Constitution of Fluorescein.** FRIEDRICH KEHRMANN and O. DENGLER [with KARL SCHEUNERT] (*Ber.*, 1909, 42, 870-879).—By the interaction of methyl sulphate and resorcinolbenzein, and of methyl sulphate and fluorescein methyl ester, the authors have been able

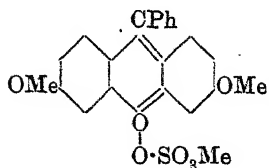


to obtain, on hydrolysis of the resulting methosulphate, oxonium bases which are strongly basic and give neutral salts.

*3-Methoxy-9-phenylfluorone* (annexed formula), prepared by the action of methyl sulphate on resorcinolbenzein in nitrobenzene solution at  $150^\circ$

and subsequent hydrolysis of the product, forms clusters of chrome-red needles, m. p. 202°. It is more strongly basic than the parent base.

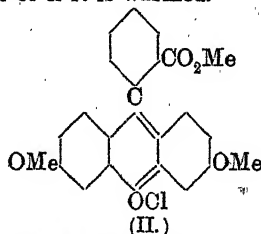
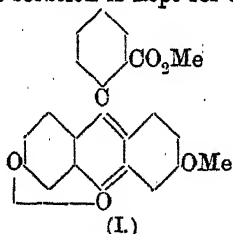
The *chloride* forms reddish-yellow prisms with a blue reflex,



and the *platinichloride* is an orange-red, crystalline powder. On methylation under the same conditions as above, 3-methoxy-9-phenylfluorone yields the *carbinol base* of 3:6-dimethoxy-9-phenylxanthylium (annexed formula: as *methosulphate*). The *chloride* forms yellow prisms or plates with a blue reflex. The *nitrate*, *iodide*, *dichromate*, *platinichloride*, *methyl ether*, m. p. 112°, and *ethyl ether*, colourless prisms, m. p. 158°, are described.

By the interaction of methyl sulphate and fluorescein methyl ester a mixture of two compounds is formed. The first, 3:6-dimethoxyfluoran,

$\text{C}_6\text{H}_4 \text{---} \text{C}(\text{CO}_2\text{Me})_2 \text{---} \text{C}_6\text{H}_3(\text{OMe})_2$ , crystallises in colourless tablets, m. p. 197°, and the second, the *phenolbetaine* of *methoxyfluorescein methyl ester* (formula I) forms brick-red needles, m. p. 176—177°. The *chloride* forms orange-red grains, and undergoes hydrolysis only when the aqueous solution is kept for a long time or if it is warmed.



Treatment of the above compound with methyl sulphate as before furnishes the *methosulphate* of *methyl 3:6-dimethoxy-9-phenylxanthylium-2'-carboxylate*, from which the *chloride* (formula II), amber-yellow prisms with a bluish-violet reflex, the *nitrate*, yellow leaflets, the *dichromate*, *iodide*, and *platinichloride* were prepared. J. C. C.

**Syntheses in the Brazan Group.** A. GRAFMANN and STANISLAUS VON KOSTANECKI (*Ber.*, 1909, 42, 822—824).—Liebermann's method for the preparation of hydroxybrazanquinones from dichloro- $\alpha$ -naphthaquinone and phenols only holds for resorcinol and, as is now found, for orcinol.

3-Hydroxy-1-methylbrazanquinone,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \text{---} \text{C}(\text{O} \cdot \text{C} \cdot \text{CO})_2 \text{---} \text{C}_6\text{H}_4$ , is

obtained in red needles, m. p. 315°, which dissolve both in dilute sodium hydroxide and in concentrated sulphuric acid with a blue coloration. The 3-acetoxy-derivative crystallises in lustrous, golden plates, m. p. 278°. If the acetylation is carried out in presence of zinc dust, the acetylated leuco-compound, 3:1':4'-triacetoxy-1-methylbrazan, is obtained; this crystallises in colourless needles, m. p. 243—244°, and is dissolved in concentrated sulphuric acid with a

green coloration and intense dark green fluorescence. 3-Methoxy-1-methylbrazanquinone, obtained on methylation with methyl sulphate, forms orange-yellow needles, m. p. 240°, which can be distilled without decomposition and dissolve in concentrated sulphuric acid with a blue coloration. When acetylated in presence of zinc dust, 3-methoxy-1-methyl-1':4'-diacetoxybrazan is formed; this separates in colourless, glistening crystals or needles, m. p. 221—222°.

The above compounds are formulated as 3-hydroxy-1-methyl derivatives, but they may with equal right be represented as 1-hydroxy-3-methylbrazanquinones. E. F. A.

**Reduction of the Thiophen Nucleus.** VICTOR THOMAS (*Bull. Soc. chim.*, 1909, [iv], 5, 182).—In connexion with the publication of a note by Padoa and Ponti (*Abstr.*, 1907, i, 146) on the reduction of the furan nucleus by hot nickel, the author points out that he is studying the reduction of the thiophen nucleus by this method, and the results so far obtained show that the reaction takes a different course from that found for furan by the Italian chemists, the ring being ruptured and benzene formed. T. A. H.

**Preparation of Leuco-derivatives.** Substituted "Thioindigotin." FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 204763).—2-Methylthiol-4-methylbenzoic acid,  $C_6H_4Me(SMe) \cdot CO_2H$ , is prepared by diazotising 4-methylanthranilic acid and treating the diazo-solution successively with potassium xanthate and sodium methyl sulphate. Methylthiolcarboxymethylbenzoic acid [4-carboxy-methylthiolacetic acid],  $CO_2H \cdot CH_2 \cdot S \cdot C_6H_4Me \cdot CO_2H$ , yellow crystals, m. p. 194—195°, is obtained by replacing sodium methyl sulphate by sodium chloroacetate in the preceding reaction. The former of these two substances yields 3-oxy-6-methylthionaphthen, m. p. 84° and 3-oxy-6-methylthionaphthencarboxylic acid on treatment with sodium-lead in the presence of alkali hydroxide at 210°; the latter gives the same products when heated at 180—190° with aqueous alkali hydroxide.

These thionaphthen derivatives when heated with sodium thio-sulphate and glycerol at 120—130° furnish the leuco-derivative of "dimethylthioindigotin," from which on oxidation the red colouring matter is produced.

The patent contains reference to other substituted "thioindigotins." G. T. M.

[Preparation of a Thioindigoid Dye from Acenaphthenequinone.] BASLER CHEMISCHE FABRIK (D.R.-P. 205377).—Acenaphthenequinone when heated with carbomethoxy-*o*-thiobenzoic acid or 2-hydroxythionaphthen, either alone or with a condensing agent, such as anhydrous sodium carbonate or sodium acetate and acetic anhydride, yields a colouring matter which crystallises from hot glacial acetic acid or benzene as a yellow or brownish-red powder. This compound probably has the following constitution:  $C_{10}H_6 \begin{matrix} \diagup CO & CO \cdot C_6H_4 \\ & C=C-S \end{matrix}$

(compare *Abstr.*, 1908, i, 979). G. T. M.

**Preparation of a Substituted  $\alpha$ -Oxythionaphthen.** KALLE & Co. (D.R.-P. 202696. Compare Abstr., 1908, i, 953).—4-Chloro-2-nitrothiophenol, when reduced with iron and hydrochloric acid and the product treated with sodium chloroacetate, gives rise to 4-chloro-2-aminophenylthiolacetic acid. The latter substance, when successively diazotised and treated with cuprous cyanide, furnishes *p*-chloro-*o*-cyanophenylthiolacetic acid, white needles, m. p. 164—165°.

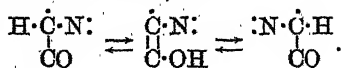
4-Chloro-2-aminothionaphthencarboxylic acid, which results from the alkaline hydrolysis of the cyano-compound, yields chloro- $\alpha$ -oxythionaphthen, white needles, m. p. 106°, when heated with dilute sulphuric acid, ammonia and carbon dioxide being simultaneously eliminated.

G. T. M.

**Partial Racemism.** ALBERT LADENBURG (*Annalen*, 1909, 364, 227—271).—A résumé of the author's publications on this subject, abstracts of which have already appeared (compare Ladenburg and Herz, Abstr., 1898, i, 296, 405; Ladenburg and Doctor, Abstr., 1898, i, 707; 1899, i, 310; Ladenburg and Bobertag, Abstr., 1903, i, 575; Ladenburg and Fischl, Abstr., 1907, i, 586; Ladenburg and Herrmann, Abstr., 1908, i, 364).

W. H. G.

**Cinchona Alkaloids. IX. Oxidation of Cinchona Alkaloids to Ketones.** PAUL RABE [with WILHELM NAUMANN and ERICH KULIGA] (*Annalen*, 1909, 364, 330—352).—It has been shown previously (Abstr., 1908, i, 100) that cinchonine contains a secondary hydroxyl group, since on oxidation it yields a ketone, namely, cinchoninone. It is now found that cinchonidine, quinine, quinidine, and hydrocinchonine, when oxidised with chromic acid, also yield ketones, and are consequently to be regarded as secondary alcohols. The ketone derived from cinchonidine is definitely proved to be identical with that obtained from cinchonine; at first sight it would appear that two stereoisomeric ketones should be formed, but it has been shown that cinchoninone is a tautomeric substance (Abstr., 1908, i, 100, 361); consequently, the stereoisomeric ketones derived from the two alkaloids are able to pass one into the other, thus:



The ketone derived from cinchonine and cinchonidine is the less soluble of these isomeric forms which crystallises from the equilibrium mixture. The fact that cinchoninone exhibits mutarotation is in agreement with this statement.

Only one ketone, namely, quininone, is obtained when quinine and quinidine are oxidised. Hydrocinchonine gives rise to hydrocinchoninone. Both these ketones exhibit mutarotation.

The final optical rotatory power of an alcoholic solution of cinchoninone from cinchonine is  $[\alpha]_D^{25} + 76.25^\circ$  ( $c = 3.279$ ),  $[\alpha]_D^{20} + 75.52^\circ$  ( $c = 3.270$ ), and from cinchonidine is  $[\alpha]_D^{25} + 72.31^\circ$  ( $c = 3.305$ ) and  $[\alpha]_D^{20} + 71.61^\circ$  ( $c = 3.3025$ ). The difference in the optical behaviour of the two specimens is due to the presence of impurity, since the methiodide of the compound from cinchonine has  $[\alpha]_D^{25} + 65.39^\circ$ .

( $c = 2.0645$  in chloroform) and from cinchonidine,  $[\alpha]_D^{15} + 65.35^\circ$  ( $c = 2.058$  in chloroform).

*Quininone*,  $C_{20}H_{22}O_2N_2$ , prepared by oxidising quinine or quinidine with chromic acid in strong sulphuric acid, crystallises in almost colourless needles or leaflets, m. p.  $101^\circ$  (heated slowly) or  $108^\circ$  (heated quickly),  $[\alpha]_D^{25} + 73.79^\circ$  (final value;  $c = 2.141$  in alcohol). It is an amphoteric substance; the *hydrochloride*,  $C_{20}H_{22}O_2N_2 \cdot HCl$ , obtained as a hygroscopic, yellow, crystalline powder, has m. p.  $210-212^\circ$ ,  $[\alpha]_D^{14} + 58.67^\circ$  (final value;  $c = 1.926$  in alcohol); the *sulphate* is an amorphous substance, m. p. about  $106-108^\circ$ ; the *picrate*,  $C_{26}H_{25}O_9N_5$ , forms canary-yellow crystals, m. p.  $232-233^\circ$ ; the *picrolonate*,  $C_{30}H_{30}O_7N_6$ , crystallises in small, yellow, prismatic needles, m. p.  $197-198^\circ$ ; the *methiodide*,  $C_{20}H_{22}O_2N_2 \cdot MeI$ , forms almost colourless, feathery crystals, m. p.  $213-214^\circ$ ; the *oxime*,  $C_{20}H_{23}O_2N_3$ , is a vitreous substance, m. p. about  $113^\circ$ .

*Hydrocinchoninone*,  $C_{19}H_{22}ON_2$ , prepared from hydrocinchonine, forms pale yellow crystals, m. p.  $138^\circ$ ,  $[\alpha]_D^{15} + 76.06^\circ$  (final value;  $c = 3.300$ ),  $[\alpha]_D^{19} + 76.22^\circ$  (final value;  $c = 2.296$ ). The *methiodide*,  $C_{19}H_{22}ON_2 \cdot MeI$ , forms small, pale yellow crystals, m. p.  $234-235^\circ$ ; the *hydrochloride*,  $C_{19}H_{22}ON_2 \cdot HCl$ , is white and sinters at  $256^\circ$ , m. p.  $265^\circ$ ; the *dihydrochloride* is very deliquescent, and could not be crystallised; the *picrate*,  $C_{25}H_{25}O_9N_5$ , forms yellow crystals, m. p.  $186^\circ$ ; the *picrolonate*,  $C_{29}H_{30}O_8N_6$ , is an orange, crystalline substance, m. p. about  $90^\circ$  (decomp.); the *oxime*,  $C_{19}H_{23}ON_3$ , is an amorphous, yellow powder, m. p.  $88-100^\circ$  (decomp.).

W. H. G.

**Preparation of Quinine and Cinchonine *p*-Aminophenylarsinates.** VEREINIGTE CHEMISCHE WERKE AKTIENGESellschaft (D.R.-P. 203081).—*Quinine p-aminophenylarsinate*, white needles, m. p.  $202^\circ$ , is obtained by double decomposition from quinine hydrochloride and sodium *p*-aminophenylarsinate. *Cinchonine p-aminophenylarsinate*, small prisms, m. p.  $180^\circ$ , is obtained similarly.

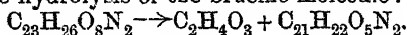
G. T. M.

**Preparation of Cotarnine Cholate.** F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 206696).—*Cotarnine cholate*, yellow powder, m. p.  $118-120^\circ$  (decomp.), readily soluble in water and alcohol, is produced by mixing cholic acid and cotarnine in water or some other suitable solvent and evaporating the solution to dryness in a vacuum at  $45^\circ$ . This compound is employed in gynaecology.

G. T. M.

**Strychnos Alkaloids. III. Reactions of Brucinonic Acid and Fission of the Brucine Molecule.** HERMANN LEUCHS and LOTHAR E. WEBER (*Ber.*, 1909, 42, 770-777. Compare *Abstr.*, 1908, i, 563; this vol., i, 120).—It has already been shown that the dibasic brucinonic acid contains two methoxyl groups and the  $>N \cdot CO$  radicle, groupings which are contained in brucine itself. The remaining oxygen atom is now shown to be ketonic, as the acid gives *brucinonic acid oxime*,  $C_{23}H_{25}O_8N_3$ , a crystalline powder, m. p.  $293^\circ$  (corr., decomp.),  $[\alpha]_D^{20} + 128.2^\circ$ , and a *semicarbazone*,  $C_{24}H_{27}O_8N_3 \cdot 3H_2O$ , which forms colourless needles, m. p.  $250-251^\circ$  (corr., decomp.),  $[\alpha]_D^{20} + 252^\circ$ . On

reduction with sodium amalgam, the semicarbazone is converted into the isomeric compound,  $C_{24}H_{27}O_8N_5$ , which forms crystals, m. p. 237—238°,  $[\alpha]_D^{20} + 128.4^\circ$ ; the nature of this derivative has not yet been elucidated. Brucinonic acid yields on reduction with sodium amalgam *brucinolic acid*,  $C_{23}H_{26}O_8N_2$ , which separates from chloroform in crystals, m. p. 250—251° (corr., decomp.),  $[\alpha]_D^{20} - 22^\circ$ ; its *acetyl* derivative has m. p. 295° (decomp.). The solution of this acid in normal sodium hydroxide (1½ mols.) gradually deposits *brucinolone*,  $C_{21}H_{23}O_5N_2$ , which crystallises from glacial acetic acid in massive prisms, m. p. 289° (corr.),  $[\alpha]_D^{20} - 32.12^\circ$ ; a molecular-weight determination in acetic acid gave 354, calc. 382; this substance is neutral. The alkaline mother liquor contains glycollic acid, and these compounds have been derived from the hydrolysis of the brucine molecule:



W. R.

**Crystallography of Pyridine Derivatives.** EVGRAF S. FEDOROFF (*Zeitsch. Kryst. Min.*, 1909, 46, 210—213; from *Verh. russ. Min. Ges.*, 1905, 43, 207—236).—2-Oximinobenzoylpyridine (two modifications: colourless, rhombic crystals and pale yellow, monoclinic crystals); 4-oximinobenzoylpyridine (monoclinic); 4-benzoylpyridine picrate (monoclinic); phenyl-2-pyridylcarbinol (rhombic); 2-benzylpyridine picrate (monoclinic); 4-benzylpiperidine platinichloride (rhombic?); 4-benzylpyridine picrate (triclinic). L. J. S.

**Resolution of the Racemic Cincholeuponic Acids into their Active Forms.** ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1909, 42, 627—633. Compare Wohl and Losanitsch, *Abstr.*, 1908, i, 47).— $\alpha$ - and  $\beta$ -Cincholeuponic acids have been resolved by the aid of brucine; the  $\beta$ -*d*-acid is identical with the acid obtained from quinine or cinchonine; a further step in the synthesis of quinine has therefore been accomplished.

Fractional crystallisation of the brucine salt of  $\alpha$ -*r*-cincholeuponic acid does not give a pure salt, but a mixture of the *r*-salt with the salt of the *l*-acid. The *l*-acid can, however, be obtained from the acid derived from this salt by crystallisation from water.  $\alpha$ -*l*-Cincholeuponic acid is anhydrous and forms prisms, m. p. 253° (corr.),  $[\alpha]_D^{20} - 35.0^\circ$  in a 4.42% solution. The *d*-acid from the syrupy filtrate of the brucine salt gave m. p. 253° and  $[\alpha]_D^{20} + 34.90^\circ$ .  $\alpha$ -*r*-Acetylcincholeuponic anhydride, prepared by boiling acetic anhydride and the hydrobromide for half an hour, crystallises from a mixture of alcohol and ether in rosettes of needles, m. p. 121°, and is converted by hot water into  $\alpha$ -*r*-acetylcincholeuponic acid,  $C_{10}H_{15}O_5N$ , which forms needles, m. p. 175° (corr.).

The  $\beta$ -acid was resolved by using the acetyl compound instead of the acid itself.  $\beta$ -*r*-Acetylcincholeuponic anhydride forms rosettes, m. p. 135—136° (corr.), and the *acid*, from anhydride and water, has m. p. 184—185° (corr.). Resolution of this acid by brucine gave the  $\beta$ -*d*-acetylcincholeuponic acid, m. p. 167—168°,  $[\alpha]_D^{20} + 19.86^\circ$ , which is identical with the compound from quinine. Hydrolysis by 20% hydrochloric acid gave  $\beta$ -*d*-cincholeuponic acid hydrochloride,  $[\alpha]_D^{20} 38.04^\circ$ , m. p. 192—194°; a crystallographic examination, showing that the

compound was identical in all respects with that obtained from cinchonine by Skraup. The *l*-hydrochloride has m. p. 192—194° and  $[\alpha]_D^{20} - 36.51^\circ$ . W. R.

**New Quinoline Derivatives and Examples of Steric Hindrance.** OTTO STARK [with FELIX HOFFMANN] (*Ber.*, 1909, 42, 715—719. Compare *Abstr.*, 1907, i, 973).—Benzoylacetone condenses with an alcoholic solution of *o*-aminobenzaldehyde in the presence of a little piperidine, yielding 3-benzoyl-2-methylquinoline,  $C_{17}H_{15}ON$ , and not 3-acetyl-2-phenylquinoline. The compound crystallises from light petroleum in well-developed prisms, m. p. 61—62°. The oxime,  $C_{17}H_{14}ON_2$ , forms colourless needles from alcohol, and has m. p. 230—231°. When distilled with potassium hydroxide and a little water, the ketone yields  $\alpha$ -quinaldine.

Dibenzoylmethane reacts with *o*-aminobenzaldehyde at 200—210°, yielding 3-benzoyl-2-phenylquinoline,  $C_{23}H_{15}ON$ , which crystallises from methyl alcohol in needles, m. p. 134—135°. It does not yield an oxime under ordinary conditions, but a 7% yield of oxime,  $C_{23}H_{16}ON_2$ , can be obtained when a large excess of hydroxylamine hydrochloride (6 mols.) and sodium hydroxide (18 mols.) are used in alcoholic solution. It has m. p. 210—211°. When decomposed by distillation with potassium hydroxide, the ketone yields 2-phenylquinoline and benzoic acid.

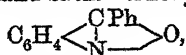
Examples of steric hindrance were noticed in the formation of the ketones, and also in the formation of the oximes. J. J. S.

**Tetrahydroacridone.** H. TIEDTKE (*Ber.*, 1909, 42, 621—626).—In analogous manner to the preparation of tetrahydroacridine from *o*-aminobenzaldehyde (*Abstr.*, 1908, i, 682), tetrahydroacridone is obtained by the condensation of anthranilic acid and cyclohexanone. In this case, however, the intermediate product can be isolated, cyclohexanone-anilino-carboxylic acid,  $CO_2H \cdot C_6H_4 \cdot N \cdot C_6H_{10}$ . It is obtained by heating the acid and the hydroaromatic ketone at 120° during one to two hours, and separates from benzene as a crystalline compound, m. p. 148°. It decomposes spontaneously on keeping, is hydrolysed by boiling water into its components, and has basic as well as acidic properties.

To prepare the tetrahydroacridone,  $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{N} \end{smallmatrix} C_6H_5$ , the anthranilic acid and cyclohexanone are heated first at 120° and afterwards at 220°. The yield is 40%, the remainder forming aniline and carbon dioxide. It crystallises from alcohol in small, colourless needles, m. p. 358°, and is easily soluble in dilute sulphuric acid, a property which can be utilised for the separation of acridone and tetrahydroacridone. It is oxidised by dry air at 280° into acridone, and distillation with zinc dust results in the formation of acridine. W. R.

**New Method of Formation of Acridone.** ALFRED KLIEGL (*Ber.*, 1909, 42, 591—594. Compare Graebe and Lagodzinski, *Abstr.*, 1892, 1086).—When 10—20 grams of *o*-nitrodiphenylmethane are carefully heated in a tubulated retort, a vigorous reaction begins at 300°. This reaction can be controlled by immersing the retort in cold sand so that the mass boils regularly; water and some *o*-nitrodiphenyl-

methane pass over, and a residue is left, which sets to a crystalline mass. When this is distilled (without thermometer), a small amount of *o*-aminobenzophenone passes over and then acridone. The reaction is less vigorous when the nitrohydrocarbon is mixed with liquid paraffin and heated on a sand-bath. Phenylanthranil,

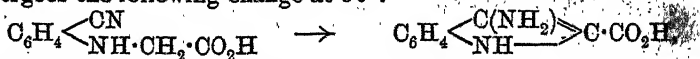


appears to be formed as an intermediate product (compare Bamberger and Elger, Abstr., 1903, i, 560), and can be isolated by means of an alcoholic mercuric chloride solution.

*p*-Tolylanthranil when heated yields 3-methyl-9-acridone,  $\text{C}_{14}\text{H}_{11}\text{ON}$ , which crystallises from glacial acetic acid in microscopic needles resembling acridone. Both compounds yield *hydrochlorides* when hydrochloric acid is added to the suspension of the compound in hot glacial acetic acid.

J. J. S.

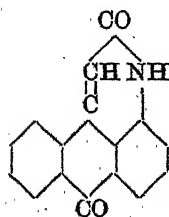
**Preparation of Indoxylcarboxylic Acid and Indoxyl.** KALLE & Co. (D.R.-P. 206903).—*o*-Nitrobenzonitrile, when reduced at low temperatures with iron and acetic or hydrochloric acid, gives a good yield of *o*-aminobenzonitrile, from which *o*-cyanophenylglycine is readily obtained. The latter, on heating with 35% sodium hydroxide, undergoes the following change at  $90^\circ$ :



and this intermediate product, when further heated with alkali at  $150$ – $220^\circ$ , loses ammonia and passes into indoxylcarboxylic acid and indoxyl, from which indigotin can be produced in the usual way.

G. T. M.

**[Preparation of Pyridones of the Anthracene Series.]** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 203752.



Compare Abstr., 1908, i, 456).—1-Acetylamino-anthraquinone, like its methyl derivative, undergoes condensation to form a pyridone when heated in nitrobenzene solution with finely-divided potassium hydroxide at  $140^\circ$ . The product, *anthrapyridone* (annexed formula), is sparingly soluble in organic media; and dissolves in concentrated sulphuric acid to a yellow, fluorescent solution. Four other compounds of this type are described in the patent.

G. T. M.

**Preparation of *p*-Phenylenediamine.** AKTIENGESSELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 202170).—*p*-Phenylenediamine is readily obtained by heating *p*-dichlorobenzene, ammonia (25%), and copper sulphate for twenty hours at  $170$ – $180^\circ$ , and finally at  $200^\circ$ .

G. T. M.

**Preparation of *p*-Phenylenediaminesulphonic Acid.** AKTIENGESSELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 202564 and 202565).—*p*-Phenylenediaminesulphonic acid is readily obtained by heating together *p*-dichlorobenzenesulphonic acid, copper chloride, and

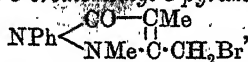
ammonia (25%) at 170°. This acid is also produced in the foregoing manner when the dichloro-acid is replaced by *p*-chloroaniline-2-sulphonic acid. G. T. M.

**Preparation of *p*-Phenylenediaminesulphonic Acid.** AKTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 202564, 204972).—*p*-Phenylenediaminesulphonic acid is obtained by heating 4-chloroaniline-3-sulphonic acid with aqueous ammonia in presence of copper salts. G. T. M.

**Preparation of 4-Amino-4'-hydroxydiphenylamine.** AKTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 204596).—The oxidation of *p*-phenylenediamine and phenol to indophenol is readily effected by hypochlorite solution in the presence of copper salts. When reduced with sodium sulphide, the indophenol gives rise to 4-amino-4'-hydroxydiphenylamine. G. T. M.

**Preparation of 1-Aryl-2:4-dialkyl-3-halogenmethyl-5-pyrazolones.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 206637).—It has been found that the 1-aryl-3-methyl-2:4-dialkyl-5-pyrazolones yield halogen additive products, which, after removal of hydrogen halide, furnish monohalogenated derivatives in which the halogen is situated in the methyl group.

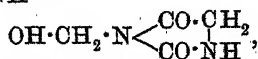
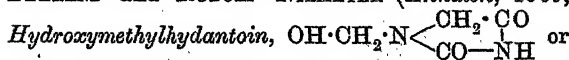
1-Phenyl-2:4-dimethyl-3-bromomethyl-5-pyrazolone,



leaflets or prisms, m. p. 113°, produced from 1-phenyl-2:3:4-trimethyl-5-pyrazolone by the successive action of bromine and sodium carbonate, yields, on boiling with water, 3-hydroxy-1-phenyl-2:3:4-trimethylpyrazolone, colourless prisms, m. p. 170°.

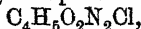
1-Phenyl-2:4-dimethyl-3-chloromethyl-5-pyrazolone, colourless crystals, m. p. 110—112°, is similarly obtained, and from 1-phenyl-2:3-dimethyl-4-ethyl-5-pyrazolone a similar series of operations leads to 1-phenyl-2-methyl-3-bromomethyl-4-ethyl-5-pyrazolone, colourless crystals, m. p. 112—113°, and 1-phenyl-2-methyl-3-hydroxymethyl-4-ethyl-5-pyrazolone, needles, m. p. 122—123°. G. T. M.

**Condensation of Hydantoin with Formaldehyde.** ROBERT BEHREND and RUDOLF NIEMEYER (*Annalen*, 1909, 365, 38—49).—



is readily prepared by heating hydantoin with 40% formaldehyde solution (1.3 mols.). It crystallises from alcohol in felted needles, m. p. 125—135°. When heated at 120—130° for several hours, it forms a clear, fused mass, which yields the compound  $\text{C}_7\text{H}_8\text{O}_4\text{N}_4$  when crystallised from hot water. The hydroxymethyl derivative is completely hydrolysed when boiled with water for an hour.

Phosphorus pentachloride, or, even better, concentrated hydrochloric acid, transforms the hydroxy-compound into *chloromethylhydantoin*,

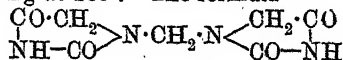


which crystallises from benzene or chloroform in well-developed prisms, m. p. 150—157°. It has not been found possible to reduce the hydroxy- or chloro-derivative to methylhydantoin.

When hydantion is warmed with formaldehyde in the presence of hydrochloric acid, complex condensation products are formed.

The compound,  $\text{C}_8\text{H}_{10}\text{O}_5\text{N}_4$ , is obtained when a few drops of concentrated hydrochloric acid are used. It crystallises from hot water in the absence of hydrochloric acid as compact, colourless prisms, m. p. 203—212°. In the presence of hydrochloric acid it yields the compound,  $\text{C}_7\text{H}_8\text{O}_4\text{N}_4$ .

This latter compound is also formed when hydantoin and formaldehyde are condensed in a strongly acid liquid. It crystallises from hot water, in which it is sparingly soluble, in lancet-shaped needles, m. p. 295°, after sintering at 285°. The formula



is suggested.

A compound,  $\text{C}_{14}\text{H}_{18}\text{O}_9\text{N}_6$ , is produced when equal volumes of concentrated hydrochloric acid and 40% formaldehyde solution are used in the condensation. It crystallises from hot water in slender prisms, m. p. 183—188°. When boiled some time with water or alcohol it loses formaldehyde, and ultimately yields the compound  $\text{C}_7\text{H}_8\text{O}_4\text{N}_4$ . In the preparation of the compound  $\text{C}_{14}\text{H}_{18}\text{O}_9\text{N}_6$ , considerable amounts of amorphous compounds are formed. When washed with alcohol, these form a hard cake, m. p. 83—85°, and readily absorb water.

J. J. S.

**Synthetical Experiments in the Iminazole [Glyoxaline] Group.** ADOLF WINDAUS (*Ber.*, 1909, 42, 758—763).—4-Methylglyoxaline condenses with formaldehyde when heated for eight hours in a closed tube at 120° to form a crumbly, hygroscopic mass, not of glyoxaline-4-ethanol, as might have been expected, but of 4-methylglyoxaline-5-carbinol. Picronic and phosphotungstic acids give precipitates with its aqueous solution; the platinichloride is difficultly soluble. Reduction of this substance with hydriodic acid gives 4:5-dimethylglyoxaline (oxalate, m. p. 261°; *picrate*,  $\text{C}_{11}\text{H}_{11}\text{O}_7\text{N}_5$ , m. p. 195°; *aurichloride*, m. p. 179—180°; *nitrate*, m. p. 175—176°; compare Künne, *Abstr.*, 1895, i, 685), a result which shows that the above conclusion is correct, as otherwise ethylglyoxaline would be formed. The methyl group in position 4 is not therefore reactive; it is the methylene group in the ring which gives the derivative, and this reaction, which is a general one for aldehydes, is not a possible method for the production of histidine derivatives. In the light of this result, doubt is thrown on the correctness of the constitution assigned by Gerngross to the product obtained from methylglyoxaline and chloral (this vol., i, 189). *Dibenzoylbutylenediamine*,  $\text{C}_8\text{H}_{18}\text{O}_2\text{N}_2$ , from dimethylglyoxaline, benzoyl chloride, and sodium hydroxide, crystallises in long needles, m. p. 241°.

Methylglyoxaline, when heated with nitric acid (D 1.5) at 80° for thirty minutes, gives a 60% yield of a *nitromethylglyoxaline*,  $C_4H_5O_2N_3$ , which crystallises from water in long prisms, decomp. 248°; solutions in ammonia or potassium hydroxide are intensely yellow, and bromine gives a *bromonitromethylglyoxaline*,  $C_4H_4O_2N_3Br$ , which forms prisms, m. p. 228° (decomp.).

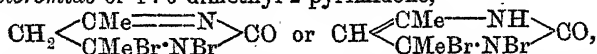
1:4-Dimethylglyoxaline gives a *nitro-derivative*,  $C_6H_7O_2N_3$ , which separates from water in long needles, m. p. 160–161°, and which does not yield alkali salts. The 2:5-dimethylglyoxaline on nitration gives 4-nitro-2:5-dimethylglyoxaline,  $CMe \begin{smallmatrix} \text{NH} & \text{CMe} \\ \diagdown & \diagup \\ \text{C}(\text{NO}_2) & \text{N} \end{smallmatrix}$ ; this forms long needles from water, m. p. 252°; its aqueous solution is neutral, but its *potassium* salt is intensely yellow, and is supposed to have the *isouminazole* constitution:  $CMe \begin{smallmatrix} \text{N} & \text{CMe} \\ \diagdown & \diagup \\ \text{C}(\text{NO}_2\text{K}) & \text{N} \end{smallmatrix}$ , a conclusion which is in harmony with the experimental fact that the 1-methyl nitro-derivative does not give a salt. W. R.

**Preparation of Pyridazine.** SIEGMUND GABRIEL (*Ber.*, 1909, 42, 654–658).—The disadvantages attending the preparation of pyridazine by the three methods already known (Täuber, *Abstr.*, 1895, i, 301; Gabriel and Colman, *ibid.*, 1899, i, 390; Marquis, *ibid.*, 1903, i, 370) are avoided by the author, who obtains the substance in quantity by the following method. An aqueous solution of  $\alpha$ -ketoglutaric acid (Blaise and Gault, *Abstr.*, 1908, i, 713) is treated with hydrazine sulphate dissolved in *N*-sodium hydroxide, and the mixture evaporated to dryness; the residue by crystallisation from hot water yields the *sodium* salt,  $C_5H_5O_3N_2Na \cdot C_5H_6O_3N_2 \cdot 2H_2O$ , from which, by boiling 10% hydrochloric acid, hydrated *pyridazinone-3-carboxylic acid*,  $CO \begin{smallmatrix} \text{NH} & \text{N} \\ \diagdown & \diagup \\ \text{CH}_2 & \text{CH}_2 \end{smallmatrix} \cdot C \cdot CO_2H \cdot H_2O$ , is obtained; this, when anhydrous, has m. p. 198°, and by treatment with bromine in glacial acetic acid yields *pyridazone-3-carboxylic acid*,  $CO \begin{smallmatrix} \text{NH} & \text{N} \\ \diagdown & \diagup \\ \text{CH} & \text{CH} \end{smallmatrix} \cdot C \cdot CO_2H$ , m. p. 259–260° (decomp.), which is changed quantitatively by fusion into 6-pyridazine,  $CO \begin{smallmatrix} \text{NH} & \text{N} \\ \diagdown & \diagup \\ \text{CH} & \text{CH} \end{smallmatrix} \cdot CH$ , m. p. 103–104°. The latter, by warming with phosphoryl chloride, yields 3-chloropyridazine, m. p. 35°, from which pyridazine is obtained by means of hydriodic acid and red phosphorus. C. S.

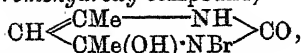
**Constitution of Acetylacetonecarbamide** [4:6-Dimethyl-2-pyrimidone]. II. Action of Bromine on Acetylacetonecarbamide and on its Benzylidene Derivatives. OTTO STARK (*Ber.*, 1909, 42, 708–714. Compare Evans, *Abstr.*, 1893, i, 129).—The dibenzylidene derivative of 4:6-dimethyl-2-pyrimidone (following abstract) readily combines with bromine in acetic acid solution, yielding a red dibromide. 4:6-Dimethyl-2-pyrimidone yields a similar yellow dibromide in chloroform solution provided that all traces of moisture are absent. In both compounds the bromine has added

itself on to a double linking in the ring. The bromides react readily with alcohol or water, yielding bromo-hydroxy- or bromo-ethoxy-derivatives. It has not been found possible to obtain tetrabromides.

The dibromide of 4:6-dimethyl-2-pyrimidone,

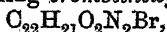


is insoluble in most organic solvents; it turns dark grey at 160°, but is not molten at 360°. When rubbed with water, the yellow colour disappears, and the bromohydroxy-compound,



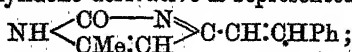
is obtained. This crystallises from alcohol in slender needles, which darken at 250°, sinter at about 330°, and decompose at 345°. The same product is obtained by the action of bromine on an acetic acid solution of the pyrimidone, and, when shaken with concentrated hydrobromic acid in the cold, yields Evans's dibromodihydroxy-derivative,  $\text{CH}_2 \begin{array}{c} \text{CMe(OH)} \cdot \text{NBr} \\ \text{CMe(OH)} \cdot \text{NBr} \end{array} \text{CO}$ . The corresponding bromo-ethoxy-derivative,  $\text{C}_8\text{H}_{13}\text{O}_2\text{N}_2\text{Br}$ , obtained by the action of ethyl alcohol on the dibromide, decomposes at 340—350°, after sintering at 330°.

The dibromide of the dibenzylidene derivative,  $\text{C}_{20}\text{H}_{18}\text{ON}_2\text{Br}_2$ , decomposes at 322—325°, after turning brown at 240° and sintering at 318°. The bromohydroxy-derivative,  $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}_2\text{Br}$ , crystallises from alcohol in orange-yellow needles, sinters at 304°, and decomposes at 310—312°. The corresponding bromoethoxy-derivative,



crystallises from alcohol in orange-yellow needles, which decompose at 308°, after sintering at 303—305°. J. J. S.

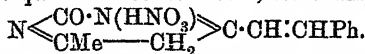
**Constitution of Acetylacetonecarbamide (4:6-Dimethyl-2-pyrimidone).** Condensation with Aromatic Aldehydes. I. OTTO STARK (*Ber.*, 1909, 42, 699—708. Compare Evans, *Abstr.*, 1893, i, 129; Combes, *ibid.*, i, 454; de Haan, *Abstr.*, 1908, i, 454).—Evans's compound condenses with alcoholic solutions of aromatic aldehydes in the presence of small amounts of piperidine. When benzaldehyde is used, a mono- and a di-benzylidene derivative are formed, and it is thus probable that it is the methyl and not the methylene hydrogen atoms which condense with the aldehydic oxygen. With *p*-hydroxybenzaldehyde and vanillin, only one molecule of aldehyde reacts. It is suggested that the condensation products are formed from the tautomeric form of the carbamide, namely, 4:6-dimethyl-2-pyrimidone; thus the monobenzylidene derivative is represented as



this is practically colourless, but the corresponding *p*-hydroxy- and hydroxymethoxy-compounds are respectively dark yellow and yellowish-brown in colour.

The salts derived from these condensation products have a much

deeper colour, namely, yellowish-red to dark red, and it is suggested that they have the quinonoid constitution, for example :



A mixture of the mono- and di-benzylidene derivatives is formed even when less than 1 gram-molecule of benzaldehyde is used for each gram-molecule of the pyrimidone, but with an excess of the aldehyde the dibenzylidene compound alone is formed. The two can be fairly readily separated, as the di-compound is only sparingly soluble in alcohol.

4-Benzylidenemethyl-6-methyl-2-pyrimidone,  $\text{C}_{13}\text{H}_{12}\text{ON}_2$ , crystallises from aqueous alcohol to which a few drops of ammonia solution have been added in slender, colourless needles, m. p. 188—189°, after sintering at 184°. The presence of the least trace of acid produces a yellow coloration.

It yields a colourless sodium salt, a yellow sulphate, an orange-yellow hydrochloride, and an orange-coloured nitrate.

The dibenzylidene derivative,  $\text{C}_{20}\text{H}_{16}\text{ON}_2$ , crystallises from boiling methyl alcohol in glistening, golden-yellow needles, which turn brown at 230°, sinter at 270°, and melt and decompose at 275°. The salts have a red colour and are sparingly soluble. The p-hydroxybenzylidene derivative,  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2$ , separates from methyl alcohol as a dark yellow, crystalline powder, m. p. 278—280° (decomp.); it dissolves in mineral acids, yielding solutions with a blood-red colour, and in sodium hydroxide to a yellow solution.

J. J. S.

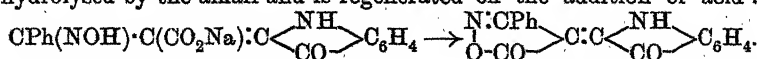
**New Synthesis of Pyrazine Derivatives by the Action of Aromatic Nitroso-o-hydroxy-compounds on Acetaldehyde in the Presence of Ammonia or Primary Aliphatic Amines.** MARTIN LANGE (*Ber.*, 1909, 42, 574—577).—An account of this work has already appeared in D.R.-P. 196563 (*Abstr.*, 1908, i, 839).

W. H. G.

**Indigoid Dyes Derived from Phenylisooxazolone.** ANDRÉ WAHL (*Compt. rend.*, 1909, 148, 352—354).—Since phenylisooxazolone behaves as though it contains the grouping  $\cdot\text{CH}_2\cdot\text{CO}$  (compare Wahl and Meyer, *Abstr.*, 1908, i, 368), it reacts with isatin chloride,

yielding 3-phenylisooxazolone-2-indole,  $\text{N}:\text{CPh} \begin{array}{c} \diagup \text{O} - \text{CO} \\ \diagdown \end{array} \text{C}:\text{C} \begin{array}{c} \diagup \text{NH} \\ \diagdown \text{CO} \end{array} \text{C}_6\text{H}_4$ ,

crystallising in garnet-red needles with a bronzy reflex. The corresponding indigoid dyes derived from the three methoxyphenylisooxazolones form reddish-brown crystals with a coppery reflex. The solutions of the compounds in aqueous sodium hydroxide or carbonate are almost colourless, and yield the parent coloured compounds on the addition of acid. It is probable that the isooxazolone nucleus is hydrolysed by the alkali and is regenerated on the addition of acid :



The yellow solutions obtained by treating the substances with

sodium hyposulphite do not yield the parent compounds when treated with acids or oxidising agents, for example, hydrogen peroxide. The *leuco*-derivatives apparently do not combine with animal or vegetable fibres.

Ethyl anisoylacetate has b. p. 189—190°/10—12 mm. (decomp.) (compare Schoonjans, Abstr., 1898, i, 425).

The following compounds were prepared: *o*-methoxyphenylisooxazolone crystallises in white needles, m. p. 106°; *m*-methoxyphenylisooxazolone forms white plates, m. p. 115°; the *p*-derivative forms white needles, m. p. 143° (compare Schoonjans, *loc. cit.*). W. H. G.

The Antique Purple Dye from *Murex brandaris*. PAUL FRIEDLÄNDER (*Ber.*, 1909, 42, 765—770. Compare Abstr., 1907, i, 867).—This dye, obtained from the above mollusc, is now shown to be 6:6'-dibromoindigotin,  $C_{16}H_8O_2N_2Br_2$ , by a direct comparison with the synthetic dye as regards its spectroscopic behaviour, colour reactions, and solubility. The influence on the colour of indigotins where positions 6 and 6' are occupied is emphasised. W. R.

Preparation of Indazyl Derivatives by means of Ortho-ketonic Hydrazines. PAUL CARRÉ (*Compt. rend.*, 1909, 148, 491—494.\* Compare Freundler, Abstr., 1904, i, 108).—The following compounds are obtained when *o*-nitrobenzophenone is reduced by zinc dust and alcoholic sodium hydroxide: (1) benzaldehyde; (2) *o*-aminobenzophenone, m. p. 110—111° (compare Geigy, Abstr., 1885, 1236); this reacts with phenylthiocarbimide giving *o*-phenylbenzophenone-thiocarbamide,  $NHPh \cdot CS \cdot NH \cdot C_6H_4 \cdot CPh$ , m. p. 156—157°; (3) 4:4'-diamino-2:2'-dibenzylidiphenyl; (4) 4:4'-diamino-2-benzylidiphenyl,  $NH_2 \cdot C_6H_4 \cdot C_6H_5(NH_2) \cdot CH_2Ph$ , white prisms, m. p. 209°; the hydrochloride decomposes at 200°; (5) a minute quantity of a white substance having the characteristic properties of an indazyl derivative.

*o*-Azobenzophenone,  $CPh \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot CPh$ , orange-red crystals, m. p. 201—202°, has been prepared by oxidising *o*-azodiphenylmethane (this vol., i, 121) with chromic acid. When treated successively with ammonium hydrosulphide and mercuric oxide it forms

2-*o*-benzophenone-3-phenylindazole,  $C_6H_4 \cdot \begin{matrix} CPh \\ \diagup \quad \diagdown \\ N \end{matrix} \cdot N \cdot C_6H_4 \cdot CPh$ , white crystals, m. p. 134—135°. W. O. W.

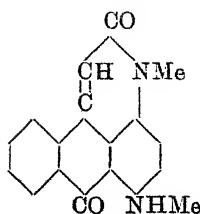
[Anthrapyridone Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205095).—Those anthrapyridones containing a halogen atom in the para-position to the imino-group readily yield *p*-arylaminoanthrapyridones on heating with aromatic bases. These products on sulphonation yield fast wool dyes.

6-*p*-Tolylamino-4-methylanthrapyridone, reddish-brown crystals, is produced by heating together 6-chloro-4-methylanthrapyridone, *p*-toluidine, and anhydrous sodium acetate.

4:6-Di-*p*-tolylaminoanthrapyridone is similarly obtained from 4:6-dichloroanthrapyridone. G. T. M.

\* and *Bull. Soc. chim.*, 1909, [iv], 5, 283—285.

**Preparation of Amino-, Alkylamino-, or Arylamino-anthrapyridones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 201904. Compare Abstr., 1908, i, 456).—The anthrapyridones which contain negative substituents in the benzene rings are readily acted on by primary or secondary bases, giving rise to amino-derivatives which are either dyes or may be employed in the production of colouring matters.

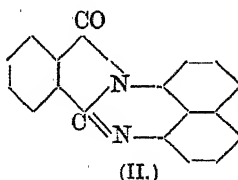
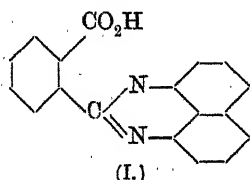


**3-Methylamino-3-methylantrapyridone** (annexed formula) separates in red crystals from a pyridine solution of methylamine and *p*-bromo-antrapyridone after heating at 120° for five hours.

**6-*p*-Tolylamino-3-methylantrapyridone** is produced by heating at 160–170° *p*-toluidine with either *p*-methoxyantrapyridone or *p*-bromo-antrapyridone; its sulphonic acid dyes wool in violet-red shades which are very fast to light.

G. T. M.

[Production of Iminazoles from 1:8-Naphthylenediamine.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 202354).—By condensing 1:8-naphthylenediamine with the polybasic acids or their anhydrides, a series of coloured condensation products of the iminazole series are obtained. Phthalic anhydride gives rise successively to the products  $C_{18}H_{12}O_2N_2$  and  $C_{18}H_{10}ON_2$ , represented respectively by formulæ I and II.



The former is a yellow compound, m. p. 185°; the latter separates from glacial acetic acid in red needles with a golden reflex, m. p. 227–228°. Similar condensation products are obtained by the use of citric acid, maleic anhydride, succinic anhydride, and *o*-benzoic sulphinide.

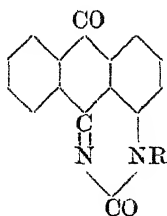
G. T. M.

**Preparation of Anthrapyrimidones.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205038).—A new class of anthracene derivatives, the anthrapyrimidones (formula I), are produced by condensing the  $\alpha$ -aminoanthraquinones or the  $\alpha$ -alkylamino-anthraquinones with urethane, alcohol and water being eliminated. The reaction is a general one.

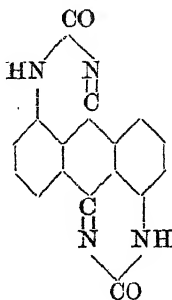
**1-Anthrapyrimidone** (with H replacing R in the formula), golden-yellow needles, m. p. above 280°, is obtained by heating together  $\alpha$ -aminoanthraquinone, urethane, and zinc chloride at 170–180°.

**1:5-Anthradipyrimidone (II)**, a brownish-red powder, is similarly

produced by heating together in nitrobenzene, 1:5-diaminoanthraquinone, urethane, and zinc chloride.



(I.)



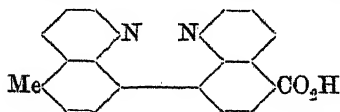
(II.)

G. T. M.

**Preparation of Anthrapyrimidones.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205914. Compare preceding abstract).—1-Anthrapyrimidone has now been prepared by condensing the  $\alpha$ -halogenated anthraquinones with carbamide in the presence of metallic salts; thus 1-bromoanthraquinone, carbamide, and copper chloride when condensed give this product together with water and hydrogen bromide.

G. T. M.

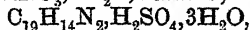
**8:8'-Diquinolylcarboxylic Acids.** ZYG. VON JAKUBÓWSKI and STEFAN VON NIEMENTOWSKI (*Ber.*, 1909, 42, 634—654).—Previous to this investigation no quinolylcarboxylic acids were known, and the first to be examined are those derived from 5:5'-dimethyl-8:8'-diquinolyl (Abstr., 1905, i, 300). The oxidation of this compound is a matter of considerable difficulty; acid or alkaline potassium permanganate, nitric acid, chromic acid in acetic acid solution, fusion with potassium hydroxide and lead peroxide were ineffective. Chromic anhydride in sulphuric acid was found to be suitable, and the mono-



or di-carboxylic acid could be obtained by altering the conditions. 5-Methyl-8:8'-diquinolyl-5'-carboxylic acid (annexed formula) was prepared by concentrating a mixture of dimethylquinolyl (1 part), 50% sulphuric acid (10 parts), and chromic anhydride (1.4 parts) at 100° until the chromic acid disappears. The purification is carried out by neutralising first with ammonia, then repeatedly crystallising the barium salt, and afterwards converting into potassium salt and recrystallising this. The acid forms a fine white, microcrystalline powder, m. p. 331—332° (decomp.), and is amphoteric in character. The following salts have been prepared: *ammonium*,  $C_{20}H_{14}N_2(NH_4) \cdot 3H_2O$ , rhombic plates which decompose at 120° into water, ammonia, and acid; *potassium*,  $C_{20}H_{13}O_2N_2K \cdot 5H_2O$ , leaflets; *barium*,  $C_{40}H_{26}O_4N_4Ba \cdot 12H_2O$ , leaflets, and a *silver* salt. Also the following: the *hydrochloride*,  $C_{20}H_{14}O_2N_2 \cdot 2HCl \cdot H_2O$ ; *nitrate*,  $C_{20}H_{14}O_2N_2 \cdot 2HNO_3$ .

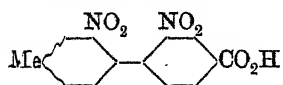
and sulphate, all of which crystallise in leaflets. 8:8'-*Diquinolyl-5:5'-dicarboxylic acid*,  $C_{20}H_{12}O_4N_2$ , is obtained from the reaction mixture of the base, chromic anhydride, and sulphuric acid after twenty-four hours at the ordinary temperature, and is purified first by conversion into the barium salt. The acid is next separated from small quantities of the monocarboxylic acid by treatment with hydrochloric acid, the monocarboxylic acid being soluble in dilute acid, whereas the dicarboxylic acid has no basic properties, and is insoluble in this menstrum. It is a microcrystalline powder, m. p.  $415^\circ$  (decomp.), and has been characterised by the *ammonium*,  $C_{20}H_{10}O_4N_2(NH_4)_2 \cdot H_2O$ , *potassium*,  $C_{20}H_{10}O_4N_2K_2 \cdot 5H_2O$ , *barium*,  $C_{20}H_{10}O_4N_2Ba \cdot 7\frac{1}{2}H_2O$ , and *silver* salts, all of which crystallise in leaflets and are more easily soluble than the corresponding monocarboxylates.

Distillation of the monocarboxylic acid under diminished pressure leads to the formation of carbon dioxide and 5-methyl-8:8'-*diquinolyl*,  $C_{19}H_{14}N_2$ , which crystallises in colourless, diagonal plates, m. p.  $211.5-212^\circ$ ; the *hydrochloride*,  $C_{19}H_{14}N_2 \cdot 2HCl \cdot 5H_2O$ , forms needles; the *nitrate*,  $C_{19}H_{14}N_2 \cdot 2HNO_3 \cdot 3H_2O$ , leaflets; *sulphate*,



leaflets, and the *platinichloride*,  $C_{19}H_{14}N_2 \cdot H_2PtCl_6$ , orange crystals. Dry distillation of the dicarboxylic acid yields an acid and a base. The acid, 8:8'-*diquinolyl-5-carboxylic acid*,  $C_{19}H_{12}O_2N_2$ , is a white, microcrystalline powder, m. p.  $310-312^\circ$ , is amphoteric in character, and is identical with the acid obtained by the oxidation of 5-methyl-8:8'-*diquinolyl* with chromic anhydride and sulphuric acid. The *ammonium*,  $C_{19}H_{11}O_2N_2(NH_4) \cdot 4H_2O$ , and *barium* salts,  $C_{19}H_{11}O_2N_2Ba \cdot 11H_2O$ , have been prepared. The base,  $C_{18}H_{12}N_2$ , forms colourless needles, m. p.  $182^\circ$  (not sharp), and is resolved by fractional crystallisation of the hydriodide into a small quantity of 8:8'-*diquinolyl* and an isomeric *diquinol*, m. p.  $187^\circ$ .

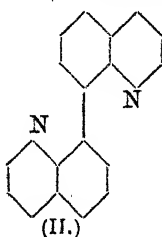
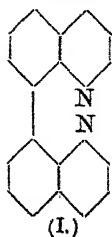
The carboxylic acid has been synthesised in the following way. Oxidation of 2:2'-*dinitro-4:4'-dimethyldiphenyl* by potassium dichromate and sulphuric acid leads to the formation of mono- and di-carboxylic acids in the ratio of 1:4. These are separated by fractional precipitation from a solution of the ammonium salts by hydrochloric acid. 2:2'-*Dinitro-4-methyldiphenyl-4'-carboxylic acid*



(annexed formula) forms crystals, m. p.  $235.5-236^\circ$ ; the *ammonium* salt, *barium* salt,  $C_{18}H_{18}O_2N_4Ba \cdot 4H_2O$ , and *silver* salt have been prepared. 2:2'-*Dinitrodiphenyl-4:4'-dicarboxylic acid*,  $C_{14}H_8O_4N_2$ , forms white crystals, m. p.  $335-337^\circ$ ; its *ammonium* salt and *barium* salt,  $C_{14}H_6O_4N_2Ba \cdot 3H_2O$ , are yellow, and the methyl ester has m. p.  $155-156^\circ$  (Ullmann and Bielecki, Abstr., 1901, i, 586, give  $159-160^\circ$ ). By the reduction of these dinitro-compounds with tin and hydrochloric acid, the corresponding diamino-derivatives are obtained. 2:2'-*Diamino-4-methyldiphenyl-4'-carboxylic acid*,  $C_{14}H_{14}O_2N_2$ , forms stout, yellow crystals, m. p.  $169-171^\circ$ ; the *hydrochloride*,  $C_{14}H_{14}O_2N_2 \cdot 2HCl$ , has m. p.  $280-285^\circ$  (decomp.), whilst 2:2'-*diaminodiphenyl-4:4'-dicarboxylic acid*,  $C_{14}H_{12}O_4N_2$ , forms very small, rhombic plates, m. p.  $307-309^\circ$ ;

its *diacetyl* derivative,  $C_{18}H_{16}O_6N_2$ , has m. p.  $250^\circ$ ; the *hydrochloride*,  $C_{14}H_{12}O_4N_2 \cdot HCl$ , is insoluble. Using arsenic acid as the oxidising agent, this dicarboxylic acid undergoes Skraup's reaction, forming 8:8'-diquinolyl-5:5'-dicarboxylic acid, apparently identical with the acid obtained from dimethyldiquinolyl, yet on dry distillation under reduced pressure, pure 8:8'-diquinolyl (m. p.  $205^\circ$ ) was obtained.

The relationships of these two isomeric diquinolyls are discussed. It is not possible to decide yet whether they are structural isomerides;

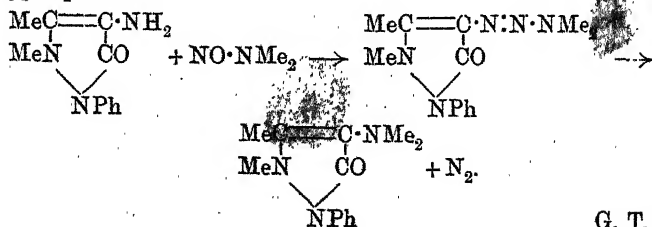


that of m. p.  $187^\circ$  might be the 8:7'- or 8:6'-modification, but this is considered to be improbable. They may be stereoisomerides of the annexed formulæ; their simultaneous production from the same dicarboxylic acid would support this, and the difference in behaviour of the acid obtained from different reactions might be accounted for by a certain fine difference between the acids themselves. Lastly,

they may be analogous to the *ana*-substituted quinoline isomerides, which have not yet been explained (Lellmann and co-workers, Abstr., 1887, 502, 737, 973; 1888, 296, 499).

W. R.

**Preparation of 4-Dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone.** SOCIÉTÉ CHIMIQUE DE L'AVANCHET (D.R.-P. 203753).—The alkylation of 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone leads to quaternary compounds, and the yield of "pyramidone" (4-dimethylamino-1-phenyl-2:3-dimethylpyrazolone) is accordingly diminished. An indirect alkylation can be effected by treating the aminopyrazolone with nitrosodimethylamine either alone at  $110^\circ$  or in the presence of copper powder:



G. T. M.

**Preparation of 5:5-Dialkyliminobarbituric Acids (5:5-Dialkylmalonylguanidines).** BASLER CHEMISCHE FABRIK (D.R.-P. 204795).—The dialkylmalonic acids can be condensed with guanidine when the acid and a salt of the base are suspended in concentrated sulphuric acid and the mixture treated with fuming sulphuric acid, chlorosulphonic acid, or phosphoric oxide.

5:5-Diethylmalonic acid and guanidine thiocyanate or hydrochloride were thus condensed to 2-imino-4:6-dioxy-5:5-diethylpyrimidine (diethylmalonylguanidine), and 2-imino-4:6-dioxy-5:5-dipropylpyrimidine was similarly prepared from 5:5-dipropylmalonic acid and guanidine hydrochloride.

G. T. M.

**Intramolecular Transformations.** OTTO DIMROTH (*Annalen*, 1909, 364, 183—226).—It has been shown previously that esters of 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylic acid readily undergo desmotropic change (compare Abstr., 1905, i, 98, 384). With the object of ascertaining whether the corresponding 5-amino-compounds behave in a similar manner, these substances have been prepared and their chemical behaviour studied. It is found that they also undergo intramolecular change when fused, yielding isomerides which, unlike the parent substances, possess acidic properties. The change under these conditions is a reversible one, but complete conversion into the acidic form may be effected by treating the neutral isomeride with sodium ethoxide or pyridine.

The velocity with which the reaction proceeds in this case, unlike that of the corresponding hydroxy-derivative, is exceedingly small. The isomeric esters when hydrolysed yield isomeric acids, which when heated evolve carbon dioxide, yielding the same acidic substance, m. p. 139°. This substance is not 5-amino-1-phenyl-1:2:3-triazole, consequently it must be derived from the ester having acidic properties. It is also found that 5-amino-1-phenyl-1:2:3-triazole and 5-amino-1:4-diphenyl-1:2:3-triazole when fused completely change into their corresponding isomerides, which are also soluble in alkalis.

Consideration of the properties of the acidic isomerides shows that these are not the result of a desmotropic change; instead, it is definitely proved that they are produced by the phenyl group changing places with a hydrogen atom of the amino-group. 1:2:3-Triazoles may be regarded as cyclic diazoamino-compounds, and this intramolecular change is similar to that which diazoamino-compounds are known to undergo when treated with bases.

The position of the imino-hydrogen atom in the ring is not yet definitely known.

[With G. WERNER.]—*Methyl 5-amino-1-phenyl-1:2:3-triazole-4-carboxylate*,  $\begin{array}{c} \text{N} \\ | \\ \text{N} \text{---} \text{NPh} \\ | \\ \text{N} \cdot \text{C}(\text{CO}_2\text{Me}) \end{array} \gg \text{C} \cdot \text{NH}_2$ , is obtained by the condensation of

phenylazoimide with methyl cyanoacetate in the presence of sodium methoxide; it crystallises in small, white needles, m. p. 173°, and is converted by boiling with pyridine or sodium ethoxide dissolved in alcohol for three hours into *methyl 5-anilino-1:2:3-triazole-4-carboxylate*,  $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_4$ , crystallising in groups of small, slender needles, m. p. 154°. The corresponding *ethyl* ester,  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_4$ , forms slender, felted needles, m. p. 129—130°; it passes into the isomeric *ethyl 5-amino-1-phenyl-1:2:3-triazole-4-carboxylate* to the extent of 33—34% in alcoholic solution and 42—44% in benzene; the *acetate*,  $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}_4$ , crystallises in needles, m. p. 90°.

[With G. WERNER and FRITZ HESS.]—*5-Amino-1-phenyl-1:2:3-triazole-4-carboxylic acid*,  $\text{C}_9\text{H}_8\text{O}_2\text{N}_4$ , formed by boiling the corresponding ester with alcoholic potassium hydroxide for thirty minutes, crystallises in small prisms, m. p. 142° (decomp.); the isomeric *5-anilino-1:2:3-triazole-4-carboxylic acid*, obtained from its ester by boiling with alcoholic potassium hydroxide for twelve to fifteen hours, crystallises in four-cornered scales, m. p. 153° (decomp.). Either of the preceding

acids when fused evolve carbon dioxide and yield 5-anilino-1-phenyl-1:2:3-triazole, and when warmed with 20% sulphuric acid yield *glycollic acid phenylamidine*,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{NHPh}$ , crystallising in colourless needles, m. p.  $130^\circ$ ; it is very unstable, and is decomposed by dilute alkalis, forming glycollanilide and ammonia.

[With J. MARSHALL and FRITZ HESS.]—1-Phenyl-1:2:3-triazole-5-carboxylic acid hydrazide,  $\text{C}_9\text{H}_9\text{ON}_5$ , obtained by heating the ester (Abstr., 1902, i, 403) with hydrazine hydrate under pressure at  $120^\circ$ , forms long, colourless needles, m. p.  $143^\circ$ ; it is converted by nitrous acid into the azoimide, glistening leaflets, m. p.  $99^\circ$  (decomp.), and by boiling ethyl alcohol into the urethane,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_4$ , colourless needles, m. p.  $98^\circ$ . The latter substance when boiled with dilute alkali yields

5-amino-1-phenyl-1:2:3-triazole,  $\begin{array}{c} \text{N}\cdot\text{NPh} \\ || \\ \text{N}-\text{CH} \end{array} \gg \text{C}\cdot\text{NH}_2$ , crystallising in needles or leaflets, m. p.  $110^\circ$ .

Methyl 5-chloro-1-phenyl-1:2:3-triazole-4-carboxylate,  $\text{C}_9\text{H}_6\text{O}_2\text{N}_3\text{Cl}$ , prepared by the action of phosphorus pentachloride on methyl 1-phenyl-5-triazolone-4-carboxylate, crystallises in a labile form, colourless needles, m. p.  $85-86^\circ$ , and a stable form, compact, rhombic crystals, m. p.  $87-88^\circ$ . It may also be obtained by the action of amyl nitrite on a solution of methyl 5-amino-1-phenyl-1:2:3-triazole-4-carboxylate in methyl alcohol containing hydrogen chloride.

5-Chloro-1-phenyl-1:2:3-triazole-4-carboxylic acid crystallises in slender, white needles, m. p.  $136^\circ$  (decomp.), and when fused yields 5-chloro-1-phenyl-1:2:3-triazole,  $\text{C}_8\text{H}_6\text{N}_3\text{Cl}$ , slender, white needles, m. p.  $50^\circ$ . The latter substance is converted by alcoholic ammonia at the ordinary temperature into 5-amino-1-phenyl-1:2:3-triazole, which, when diazotised and coupled with  $\beta$ -naphthol, yields 1-phenyltriazole-5-azo- $\beta$ -naphthol,  $\text{C}_{18}\text{H}_{13}\text{ON}_5$ , crystallising in red plates, m. p.  $215^\circ$  (decomp.).

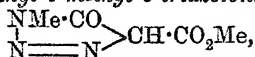
5-Anilino-1-phenyl-1:2:3-triazole,  $\text{C}_8\text{H}_8\text{N}_4$ , prepared by fusing 5-amino-1-phenyl-1:2:3-triazole or as described above, crystallises in large, glistening leaflets, m. p.  $139^\circ$ ; it forms a silver salt,  $\text{C}_8\text{H}_7\text{N}_4\text{Ag}$ , and a hydrochloride, m. p.  $128^\circ$ ; the acetate,  $\text{C}_{10}\text{H}_{10}\text{ON}_4$ , crystallises in white needles, m. p.  $137-138^\circ$ ; the urethane,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_4$ , forms white leaflets, m. p.  $147^\circ$ ; the nitroso-derivative,  $\text{C}_8\text{H}_7\text{ON}_5$ , forms yellow crystals, m. p.  $115-116^\circ$  (decomp.).

5-Amino-1:4-diphenyltriazole (compare Dimroth and Werner, Abstr., 1903, i, 127), when diazotised and coupled with  $\beta$ -naphthol, yields 1:4-diphenyltriazole-5-azo- $\beta$ -naphthol,  $\text{C}_{24}\text{H}_{17}\text{ON}_5$ , red needles, m. p.  $204^\circ$ . The diazo-solution when treated with cuprous chloride yields 5-chloro-1:4-diphenyltriazole (compare Abstr., 1905, i, 98).

[With FRITZ HESS.]—5-Anilino-4-phenyltriazole,  $\text{C}_{14}\text{H}_{12}\text{N}_4$ , prepared by boiling 5-amino-1:4-diphenyltriazole with pyridine, crystallises in needles, m. p.  $167^\circ$ ; it forms salts with alkalis and acids.

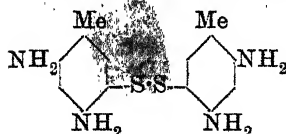
5-Methylamino-1-phenyl-1:2:3-triazole,  $\text{C}_9\text{H}_{10}\text{O}_4$ , is obtained by the action of methylamine on 5-chloro-1-phenyltriazole; it crystallises in slightly yellow, compact prisms, m. p.  $102^\circ$ , and when boiled with water or pyridine passes into 5-anilino-1-methyl-1:2:3-triazole,  $\text{C}_9\text{H}_{10}\text{N}_4$ , white leaflets, m. p.  $172^\circ$ .

*Methyl 5-hydroxy-1-methyltriazole-4-carboxylate*,  $C_5H_7O_3N_3$ , prepared by the action of methylazoimide on methyl malonate in the presence of sodium methoxide, forms hexagonal crystals, m. p.  $136^\circ$ ; when fused, it passes into *methyl 1-methyl-5-triazolone-4-carboxylate*,

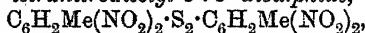


crystallising in yellow needles, m. p.  $75^\circ$ . Either the enolic or ketonic ester when treated with phosphorus pentachloride yields *methyl 5-chloro-1-methyltriazole-4-carboxylate*, crystallising in long, white leaflets, m. p.  $112^\circ$ ; the corresponding *acid* crystallises in white needles, m. p.  $167^\circ$ , and passes into 5-chloro-1-methyl-1:2:3-triazole when fused, which substance when treated with aniline yields 5-anilino-1-methyl-1:2:3-triazole, identical with that just described. 5-Chloro-1-phenyl-1:2:3-triazole is converted by aniline into 5-anilino-1-phenyltriazole,  $C_{14}H_{12}N_4$ , small, glistening, square plates, m. p.  $142^\circ$ , and by sodium ethoxide at the ordinary temperature into 5-ethoxy-1-phenyl-1:2:3-triazole (compare Abstr., 1905, i, 98). W. H. G.

**Action of Sulphur on *m*-Tolylenediamine.** I. and II. GUSTAV SCHULTZ and HEINRICH BEYSCHLAG (*Ber.*, 1909, 42, 743—752, 753—757).—*m*-Diamines are characterised by the ease with which elementary sulphur is introduced into the molecule. The gentle boiling of alcoholic *m*-tolylenediamine and sulphur for five to six hours leads to the evolution of hydrogen sulphide and the formation of a mixture of polysulphides, from which *dithio-m-tolylenediamine* (annexed formula), m. p.  $215^\circ$ , has been isolated in tufts of yellow needles by fractional crystallisation from alcohol. The constitution of the disulphide is proved from its formation by the reduction with stannous chloride and hydrochloric acid of 2:3:2':3'-tetranitroditolyl 5:5'-disulphide,

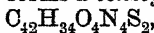


acid of 2:3:2':3'-tetranitroditolyl 5:5'-disulphide,



which decomposes before melting at  $265^\circ$ , and is obtained by the action of an alcoholic solution of crystallised sodium sulphide on alcoholic 5-chloro-2:4-dinitrotoluene.

Dithio-*m*-tolylenediamine forms a *benzoyl* derivative,

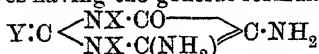


and a *benzylidene* compound,  $C_{42}H_{34}N_4S_2$ , m. p.  $152$ — $153^\circ$ , yields 4-acetylamino-1:5-dimethylbenzthiazole, m. p.  $180$ — $181^\circ$ , by warming with zinc dust, glacial acetic acid, and acetic anhydride, and gives, by treating its solution in dilute hydrochloric acid with hydrogen sulphide, 2:4-diamino-*m*-tolyl mercaptan, which forms yellow needles, and, on account of its extreme oxidisability, is best kept in the form of the *hydrochloride*,  $C_7H_{10}N_2S_2 \cdot 2HCl$ .

Since dithio-*m*-tolylenediamine dissolved in boiling alcohol takes up, per mol., six atoms of sulphur without evolution of hydrogen sulphide, giving a mixture of polysulphides, whilst 2:4-diamino-*m*-tolyl mercaptan under similar conditions combines with sulphur with the evolution of hydrogen sulphide, giving the same mixture of polysulphides, it is probable that the entrance of sulphur into *m*-tolylene-

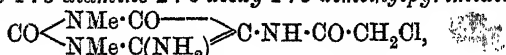
diamine is due to the initial formation of the mercaptan, which then changes into the disulphide, to which the addition of sulphur leads to the formation of higher unstable polysulphides. These polysulphides then react with the unchanged base and with the intermediately formed mercaptan to give the mixture of lower stable polysulphides which is ultimately isolated. C. S.

**Preparation of *o*-Diaminopyrimidines containing Halogenated Acyl Groups.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206454).—It has now been found that 4:5-diaminopyrimidine derivatives having the general formula



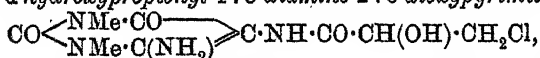
(where X is hydrogen or an alkyl group and Y an oxygen or sulphur atom, or an imino- or a cyanimino-group) readily react with halogenated carboxy-acids to give derivatives with an acyl group in position 5.

*5-Chloroacetyl-4:5-diamino-2:6-dioxy-1:3-dimethylpyrimidine*,



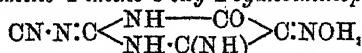
white crystals, m. p. 210°, is produced by heating together at 120° chloroacetic acid and 4:5-diamino-2:6-dioxy-1:3-dimethylpyrimidine.

*β-Chloro-α-hydroxypropionyl-4:5-diamino-2:6-dioxy-1:3-dimethylpyrimidine*,



m. p. 215°, is obtained in a similar manner by replacing chloroacetic by β-chlorolactic acid in the foregoing condensation. G. T. M.

**Preparation of 5-Oximino-4-iminopyrimidine Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206453).—5-Oximino-4-imino-2:6-dioxy-1:3-dimethylpyrimidine is produced by condensing ethyl oximinocynoacetate and carbimide with sodium ethoxide in absolute alcohol. A similar condensation between ethyl oximinocynoacetate, dicyanodiamide, and potassium ethoxide leads to the formation of 5-oximino-4-imino-6-oxy-2-cyanoiminopyrimidine,



red needles, insoluble in water and the organic media, but yielding sparingly soluble salts with aqueous alkalis. Other condensations with ethyl oximinocynoacetate are indicated in the patent, but the products have already been described (compare Abstr., 1900, i, 416; 1901, i, 54).

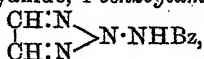
G. T. M.

**Derivatives of Osotetrazine and of Osotriazole.** HANS VON FECHMANN and WILHELM BAUER (*Ber.*, 1909, 42, 659–674).—By oxidising the dibenzoylhydrazones of diacetyl and of glyoxal to the corresponding dibenzoylosotetrazines and hydrolysing the latter, the authors hoped to obtain osotetrazine and its dimethyl homologue. The hydrolysis of the dibenzoylosotetrazines, however, yields the corresponding amino-osotriazoles, and thus furnishes another addition to the several recent instances of the conversion of tetrazines into amino-triazoles. Consequently, the substances described previously (Abstr.,

1900, i, 314) as benzoyldimethylsotetrazine and dimethylsotetrazine are 1-benzoylamino-3:4-dimethyl-1:2:5-triazole, m. p. 95°, and 1-amino-3:4-dimethyl-1:2:5-triazole, m. p. 95°, respectively. The evidence for the constitutions of the two compounds is the following: (1) By benzoylation the original dibenzoyldimethylsotetrazine is not reproduced, but Stollé's 1-dibenzoylamino-3:4-dimethyl-1:2:5-triazole, m. p. 115° (this vol., i, 123); (2) the formation of the *benzylidene* compound,  $\begin{smallmatrix} \text{CMe:N} \\ \text{CMe:N} \end{smallmatrix} > \text{N:N:CHPh}$ , m. p. 80°; (3) by the action of nitrous acid aminodimethyl-1:2:5-triazole yields 3:4-dimethyl-1:2:5-triazole, m. p. 70° (with 3H<sub>2</sub>O, m. p. 97°), the constitution of which is proved by nitrating 1-phenyl-3:4-dimethyl-1:2:5-triazole (Abstr., 1888, 1287) in the cold, reducing the *nitro*-compound, C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>N<sub>4</sub>, m. p. 227°, to 1-aminophenyl-3:4-dimethyl-1:2:5-triazole,  $\begin{smallmatrix} \text{CMe:N} \\ \text{CMe:N} \end{smallmatrix} > \text{N:C}_6\text{H}_4\text{NH}_2$ , m. p. 132°, and oxidising the latter by potassium permanganate and dilute sulphuric acid, whereby 3:4-dimethyl-1:2:5-triazole, identical with the preceding, is obtained.

An aqueous solution of diacetyl and benzhydrazide yields *diacetylbenzoylhydrazone*, CH<sub>3</sub>·CO·CMe:N·NHBz, m. p. about 167° (completely at 185°), which by recrystallisation from hot glacial acetic acid gives *diacetylbenzoylosazone*, NHBz·N:CMe·CMe:N·NHBz, m. p. 286·5° (decomp.), which is also obtained by heating an excess of alcoholic benzhydrazide and diacetyl for six hours at 100°. The osazone by oxidation with alkaline 25% potassium ferricyanide yields Stollé's 2:3-dibenzoyl-5:6-dimethyl-1:2:3:4-tetrazine (*loc. cit.*), m. p. 140°, which differs from the corresponding diphenyltetrazine in being colourless and in not being capable of reduction to the osazone. By hydrolysis with concentrated hydrochloric acid the dibenzoyldimethyltetrazine yields 1-benzoylamino-3:4-dimethyl-1:2:5-triazole. 1-Amino-3:4-dimethyl-1:2:5-triazole, obtained by hydrolysing the preceding compound in a sealed tube, forms a *hydrochloride*, m. p. 131°, *mercurichloride*, m. p. 145°, *picrate*, m. p. 124—125°, and a *platinichloride*, decomposing at 215°; it is unaffected by mild oxidising agents, is converted into diacetyl by potassium dichromate or lead peroxide and sulphuric acid, and yields βγγ-tetrabromobutane by the action of bromine water.

Compounds similar to the preceding have been obtained from glyoxal. When the sodium hydrogen sulphite compound is heated with dilute sulphuric acid until sulphur dioxide is eliminated, the solution treated with an excess of sodium acetate, and heated with benzhydrazide, *glyoxalbenzoylosazone*, NHBz·N:CH·CH:N·NHBz, is obtained as a white powder, which melts above 300°, and gives, by oxidation with alkaline potassium ferricyanide, 1-benzoylamino-1:2:5-triazole,



m. p. 151°, which by hydrolysis with dilute hydrochloric acid in a sealed tube at 90—100° yields 1-amino-1:2:5-triazole, m. p. 51° (*picrate*, m. p. 130°, decomp.; *hydrochloride*, m. p. 114°, decomp.), from which Pechmann's osotriazole is obtained by the action of nitrous acid. C. S.

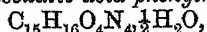
**Oxidation of Uric Acid in Alkaline Solution.** ROBERT BEHREND and ROLAND SCHULTZ (*Annalen*, 1909, 365, 21—37).—Attempts have been made to confirm the conclusion previously drawn (Abstr., 1904, i, 950), namely, that hydroxyglycurilcarboxylic acid is first formed during the oxidation, and that this is transformed partly into uroxic acid and partly into a substance which yields allantoin when acidified.

When a larger quantity of permanganate was used, the chief product was biuret together with a small amount of the potassium salt of a *dibasic acid*,  $C_5H_7O_4N_5$ . It is possible that the latter compound was formed by the oxidation of guanine contained in the crude uric acid.

Attempts have been made to establish the constitution of uroxic acid. Behrend's formula (*loc. cit.*), namely, diureidomalonic acid,  $C(CO_2H)_2(NH \cdot CO \cdot NH_2)_2$ , is supported by a study of the alkali salts and also by the behaviour of the acid towards methyl alcohol. The normal potassium salt is neutral to litmus and phenolphthalein in aqueous solution, whereas the acid potassium salts of diureides of the type of uric acid are distinctly alkaline. The behaviour of the normal salts is thus completely in harmony with the view that uroxic acid is a substituted malonic acid containing two carboxyl groups. The readiness with which the acid loses carbon dioxide and yields allantoic acid when shaken for several days with cold 95% methyl alcohol is also in harmony with this formula, whereas Medicus' formula (*Ber.*, 1876, 9, 462) would necessitate the rupture by cold methyl alcohol of a ring which is stable even in the presence of concentrated alkali.

*Normal phenylhydrazine uroxanate*,  $C_5H_8O_6N_4 \cdot 2C_6H_5N_2$ , crystallises in colourless plates, m. p. 130—132° (decomp.), after turning yellow at 120°. Aniline and hydroxylamine also yield sparingly soluble salts; the latter has m. p. 155° (decomp.).

When boiled with water the phenylhydrazine uroxanate yields the phenylhydrazine salt of *mesoxalic acid phenylhydrazone*,



which crystallises in yellow needles. It darkens at 140—150°, melts at 154—158°, solidifies again at 160°, and melts a second time at 183° (decomp.). Hydrochloric acid decomposes this salt, yielding *mesoxalic acid phenylhydrazone*,  $C_9H_8O_4N_2$ , which crystallises in minute needles, m. p. 170—171° (decomp.).

When heated with water, uroxic acid yields allanturic acid, mesoxalic acid, and carbamide.

J. J. S.

**Production of Azoxy- and Azo-compounds of the Benzene Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 204653).—The sulphides of the heavy metals can be employed in the production of the reduction products of nitrobenzene. This substance when boiled with iron pyrites and 60% aqueous sodium hydroxide yields about 90% of azoxybenzene. When the reaction is carried out at 140°, further reduction occurs and 85—90% of azobenzene is obtained.

G. T. M.

**p-Nitrodiazobenzene Chloride.** HANS T. BUCHERER and S. WOLFF (*Ber.*, 1909, 42, 881—887).—In preparing a nitrous acid-free

solution of *p*-nitrodiazobenzene by acidifying the sodium isodiazotate ("nitrosamine" paste), the authors noticed that the solution always showed the presence of free nitrous acid, and the paste, when acidified with acetic acid instead of hydrochloric acid, gave this reaction only after some time. The conclusion is drawn that the nitrous acid is produced by the hydrolytic decomposition of the diazonium hydroxide into nitrous acid and *p*-nitroaniline. After proving that excess of nitrous acid in a diazo-solution can be removed by means of hydrogen peroxide or potassium permanganate (whereby it is oxidised to nitric acid), the authors investigated the action of various reagents on a solution of *p*-nitrodiazobenzene chloride in order to ascertain if, on slowly liberating the diazonium hydroxide, the above reaction would proceed, which would be shown by the combination of the *p*-nitroaniline with some of the diazo-salt present to form the corresponding diazoamino-compound. The addition of solutions of sodium hydroxide, hydrogen carbonate, carbonate, acetate, ammonia, ammonium carbonate, soap, or a mixture of soap and sodium carbonate gave rise to the formation of a diazoamino-compound in varying degrees, but with ammonium acetate an almost quantitative yield of *p*-dinitrodiazoaminobenzene was obtained. It is considered that this is due to the rapid removal of the nitrous acid liberated in the hydrolysis owing to the formation of ammonium nitrite, which at once decomposes. The addition of ammonium chloride or carbamide to the diazo-solution produced no appreciable effect. Preliminary experiments with diazotised sulphanilic acid and *o*-nitrodiazobenzene chloride showed that the reactions do not proceed quite in the same way as those described above.

J. C. C.

**Preparation of *p*-Aminodiazobenzene and its Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205037).—Acetyl-*p*-phenylenediamine is diazotised with sodium nitrite in hydrochloric acid, a further quantity of hydrochloric acid is added, and the sodium heated at 70° for one hour. At the end of this time the solution no longer gives the azo-coupling reaction with sodium  $\beta$ -naphthol-3 : 6-disulphonate (*R* salt) in cold aqueous sodium carbonate. This diazo-solution now contains *p*-aminodiazobenzene, which only gives an azo-derivative with *R* salt either very slowly at the ordinary temperature or more rapidly on warming.

G. T. M.

**Iodothyreoglobulin.** A. NÜRENBERG (*Biochem. Zeitsch.*, 1909, 16, 87—110).—Iodothyreoglobulin is the name given by Oswald to the protein substance in the colloid matter of the thyroid gland which contains iodine. The elementary analyses given are very like those of Oswald. Among its hydrolytic cleavage products, arginine, histidine (?), lysine, tyrosine, glutamic acid, glycine, alanine, leucine, phenylalanine, aspartic acid, and proline were separated. The iodine is united to the aromatic groups, especially to tyrosine and tryptophan.

W. D. H.

**Partial Hydrolysis of Certain Proteins.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1909, 58, 373—389).—The distinction

the linoleic series. In the present research it was obtained in crystalline form, m. p.  $122^{\circ}$ ; its identification is not yet completed; its elementary composition gives figures lying between those required by the formulæ  $C_{19}H_{38}O_4$  and  $C_{18}H_{36}O_4$ . W. D. H.

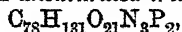
**Preparation of Glucothionic Acid.** PHOEBUS A. LEVENE (*Biochem. Zeitsch.*, 1909, 16, 246—249. Compare Mandel and Neuberg, Abstr., 1908, i, 1029).—Details are given of a modified method for the purification of glucothionic acids, more especially for the removal of nucleic acids.

The analysis of an acid barium salt agreed fairly well with the formula  $(C_{14}H_{20}O_{14}NS)_2Ba \cdot 2H_2O$ . J. J. S.

"Glucothionic Acids." CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 16, 250—253).—A reply to Levene (preceding abstract). Largely polemical. The conclusions arrived at previously (Abstr., 1908, i, 1029) are adhered to. J. J. S.

**Lipoids. II. Unsaturated Phosphatides of the Kidney.** SIGMUND FRÄNKEL and ALEXANDER NOGUEIRA (*Biochem. Zeitsch.*, 1909, 16, 366—377. Compare Abstr., 1908, i, 377).—Three unsaturated phosphatides have been prepared from the ox-kidney. One of these, present in only small quantity, has the properties of kephalin; when dry it is dark yellow and of a waxy consistence; it begins to melt at  $125^{\circ}$  and decomposes at  $135^{\circ}$ . The Hübl iodine number is 70·38.

The second compound, an *unsaturated triaminodiphosphatide*,



is precipitated from the extract of the kidneys after removal of the kephalin as a *cadmium* compound,  $C_{78}H_{181}O_{21}N_3P_2 \cdot 2HCl \cdot 2CdCl_2$ . The free phosphatide is dibasic in character, and has iodine number 82, whilst that of the cadmium compound is 63·48. Two of the nitrogen atoms are in the form of choline, that is, combined with methyl groups. It is a pale yellow powder, m. p.  $205^{\circ}$ , and optically inactive in dilute ethereal solution.

Lastly, a *diaminomonophosphatide*, found in small quantities, has no basic properties, but forms a *cadmium* salt,  $C_{34}H_{74}O_{10}N_2P \cdot 2CdCl_2$ , m. p.  $215^{\circ}$ , which has an iodine value of 25·81 and is much less unsaturated than the previous compound; the free phosphatide has a value of 37·83. Only one of the nitrogen atoms is in the form of choline. E. F. A.

**Lipoids. III. Interaction between the Unsaturated Phosphatides of the Kidney and Dyes.** SIGMUND FRÄNKEL and ALEXANDER NOGUEIRA (*Biochem. Zeitsch.*, 1909, 16, 378—382).—Dyes are excreted by the kidney in a changed state, methylene-blue, for example, being converted into a leuco-derivative. The behaviour of the three unsaturated phosphatides of the kidney (see previous abstract), which have a marked affinity for oxygen, towards methylene-blue has been studied outside the organism.

Triaminodiphosphatide decolorises methylene-blue slightly in the cold, more strongly on heating to  $50^{\circ}$ . The blue colour does not re-

appear on shaking with air, but is reformed to some extent, although not entirely on adding acetic acid or on boiling. Chloroform extracts from the reduced liquid the same soluble methylene-blue as occurs in human urine after administration of the dye. The leuco-derivative corresponds with the chromogen of Voisin and Hauser.

The diaminomonophosphatide reduces methylene-blue strongly to a chromogen, but the primary colour is completely restored on adding acetic acid and boiling.

The kephalin-like substance produces a greenish-blue solution. The original colour is not restored on shaking with air, but a clouded blue liquid is produced by boiling with acetic acid. A similar green dye is often found in dog's urine after administration of methylene-blue, but seldom in human urine.

None of the phosphatides react with indigo-carmin. The most completely saturated of the three has the strongest decolorising action towards methylene-blue.

E. F. A.

**Plasteins. II.** PHCEBUS A. LEVENE and DONALD D. VAN SLYKE (*Biochem. Zeitsch.*, 1909, 16, 203—206. Compare Abstr., 1908, i, 932).—The viscosity of plastein solutions in alkali is less than that of native proteins, and is nearly as low as that of Witté's peptone. The viscosity sinks slightly after a short time and then remains practically constant. The viscosity of such native proteins as fibrin sinks more gradually and continues to fall until lower than that of plastein. Whether plastein is a decomposition product of protein cleavage which settles out on account of its insolubility or whether it is synthetically formed from secondary proteoses is left uncertain.

W. D. H.

**Mechanical Destruction of Pepsin.** A. O. SHAKLEE and SAMUEL J. MELTZER (*Proc. Amer. Physiol. Soc.*, 1908, xxix—xxx; *Amer. J. Physiol.*, 23).—Shaking a solution of pepsin at room temperature diminishes its activity and finally destroys it. This action is more rapid at 33°. It is not due to oxidation, but occurs just the same in inert gases. Mere shaking in the animal body lessens its strength, as was determined by introducing a small bottle of pepsin solution into a dog's stomach.

W. D. H.

**Electrical Transportation of Ferments. I. Invertin.** LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 16, 81—86).—In order to avoid injurious changes in reaction, unpolarisable electrodes (zinc in solutions of zinc sulphate) were employed. The experiments were made in a U-tube, the bend of which, containing the ferment, could be closed by taps and so separated from the side-tubes which contained water. The latter were fitted with glass tubes containing the electrode, and zinc sulphate.

Results obtained both without, and in presence of, acetic acid showed that, as indicated by the absorption method, invertin is an acid.

N. H. J. M.

**Enzymes which Hydrolyse (1) Salicin and (2) Arbutin.** WILHELM SIGMUND (*Monatsh.*, 1909, 30, 77—87).—The leafy twigs of

various species of *Salix* and *Populus* contain an enzyme which is capable of hydrolysing salicin to dextrose and saligenin; this the author names *salikase*. The action of the enzyme, which differs from emulsin, was shown by autolytic experiments and by means of the precipitate obtained on adding alcohol to the aqueous extract of the twigs.

Similarly, the twigs of *Calluna vulgaris* and of *Vaccinium Myrtillus* contain an enzyme, to which the name *arbutase* is given, capable of hydrolysing arbutin into quinol and dextrose. T. H. P.

**Basiphil Rennets.** C. GERBER (*Compt. rend.*, 1909, 148, 56—58).—As a result of the study of the time of clotting of milk produced by rennets of different origin in the presence of varying quantities of acids and alkalis, the conclusion is drawn that there are two extreme types of rennet, namely, oxyphil and basiphil. The former include the rennets from calf and pig, the latter those from *Machura* and the decapod crustaceans. Between the extreme types, there are other rennets which can be classified according to their action in the presence of various mineral and organic acids. S. B. S.

**Rennet Action.** W. VAN DAM (*Zeitsch. physiol. Chem.*, 1908, 58, 295—330).—The investigation was undertaken to determine why certain specimens of cow's milk do not readily curdle with rennet. It was found by the electrical conductivity method that the coagulation-time is inversely proportional to the hydrogen ions present. The main reason of want of satisfactory curdling is poorness in calcium salts, and this can be corrected by giving the cows calcium phosphate in their food. W. D. H.

**Theory of the Curdling of Milk by Rennet.** GERHARD WERNCKEN (*Zeitsch. Biol.*, 1908, 52, 47—71).—Differences in the internal friction of solutions of caseinogen and casein (called in the paper casein and paracasein respectively) are so small as to be within the errors of analysis. Caseinogen solutions show a tryptophan reaction after a comparatively short lapse of time; nevertheless, the theory that casein is the result of fermentative change in caseinogen is considered untenable. W. D. H.

**Coagulation of Fresh Milk by the Rennet of the Papaw Tree (*Carica Papaya*).** C. GERBER (*Compt. rend.*, 1909, 148, 497—500).—The rennet in papayotin-Merck is much more resistant to high temperatures than that of yeast and of pepsin, and clots milk at 0° even when calcium is absent. The product of the quantity of ferment by the time taken to clot a given quantity of milk remains constant when the milk is perfectly fresh, but when the milk is four hours' old it clots too slowly with small quantities of ferment, so that the above-mentioned product increases when the quantity of ferment is diminished. G. B.

**Tyrosinase.** ALEXIS BACH (*Ber.*, 1909, 42, 594—601. Compare Abstr., 1906, i, 616; 1907, i, 268, 810; 1908, i, 237, 746).—Numerous

experiments which have been made do not support Gonnermann's hypothesis (*Pflüger's Archiv*, 1900, 82) that tyrosinase is a hydrolysing enzyme and that the products of hydrolysis of tyrosine are subsequently oxidised by atmospheric oxygen. Gessard's view (*Abstr.*, 1900, i, 468) that the specific action of tyrosinase is due to the presence of certain metallic salts is also shown to be untenable.

Experiments with some hundred different plant-juices and extracts prove that the oxidation of tyrosine by means of peroxydase, hydrogen peroxide, and a plant-juice or ferment preparation takes place only when the juice or preparation itself oxidises the base, namely, contains tyrosinase. In many cases the activity of the tyrosinase is concealed by the presence of reducing substances, but when these are removed by precipitation with alcohol, the activity of the tyrosinase can be demonstrated.

The activity of purified tyrosinase towards tyrosine is appreciably diminished by the addition of neutral peroxydase, whether hydrogen peroxide is present or not. If the plant extract or tyrosinase preparation contains reducing or other substances which lower its activity, the addition of peroxydase and hydrogen peroxide produces an initial acceleration in the oxidation, but after a short time the inhibiting action of the peroxydase can be noticed. This initial acceleration is not due to the oxidation of the tyrosine, but to the decomposition of the reducing or other substances present.

J. J. S.

**Artificial Oxydases and Peroxydases.** V. MARTINAND (*Compt. rend.*, 1909, 148, 182).—The oxides of alkalis and alkaline earths which form soluble peroxides and percarbonates give reactions similar to organic peroxydase. Salts of metals which form several peroxides react in a similar way when they correspond with the higher oxides of the metal; those corresponding to the lower oxides do not act in this manner.

S. B. S.

**Action of Acids on Peroxydase.** GABRIEL BERTRAND and M<sup>lle</sup>. M. ROZENBAND (*Compt. rend.*, 1909, 148, 297—300. Compare *ibid.*, 1907, 145, 340).—In the case of laccase and tyrosinase, certain acids inhibit the ferment in minute doses, whilst other acids are almost without effect. As regards the action of acids in peroxydase (from wheat-bran), no such division into two groups can be traced, the inhibitory effect being of the same order of magnitude as the electrical conductivity, although not proportional to it.

G. B.

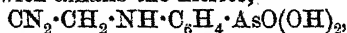
**Some New Properties of the Oxydases of *Russula Delica*.** JULES WOLFF (*Compt. rend.*, 1909, 148, 500—502).—The oxydase from *Russula Delica* is most active on tyrosine and many other substances when the solution is neutral to phenolphthalein. Some colouring matters are oxidised both by this oxydase and by laccase, but others are only oxidised by the ferment from *Russula*.

G. B.

**Preparation of Hydroxyarylsarsinic Acids.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205616).—*p*-Hydroxyphenylarsinic acid,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$ , yellow prisms, m. p. 173—174°.

has now been prepared directly from phenol and crystallised arsenic acid by heating at  $150^{\circ}$  for four hours. The product soluble in water is evaporated to dryness, and the arsenic acid extracted from the residue with acetone. 4-Hydroxy-3-tolylarsinic acid is similarly obtained from *o*-cresol and arsenic acid at  $140^{\circ}$ . With *m*-cresol and arsenic acid the reaction takes place at  $170^{\circ}$ . 4-Hydroxy-2-tolylarsinic acid,  $\text{HO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{AsO}(\text{OH})_2$ , sinters at  $160^{\circ}$  and decomposes at  $183\text{--}185^{\circ}$ .  
G. T. M.

**Preparation of *p*-Arylglycinearsinic Acids.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 204664).—*Phenylglycine-p*-arsinic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$ , is prepared either by mixing sodium *p*-aminoarsinate and chloroacetic acid in hot water or by hydrolysing with alkalis the nitrite,



produced by warming together in aqueous solution, *p*-aminophenylarsinic acid, potassium cyanide, and formaldehyde (40%).

G. T. M.

**Preparation of Sulphur Derivatives of *p*-Aminophenylarsinic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 205617).—*p*-Aminophenylarsenious sulphide,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsS}$ , yellowish-white powder, m. p.  $180^{\circ}$ , is obtained by passing hydrogen sulphide into an acidified solution of *p*-aminophenylarsinic acid. The free sulphur is removed by carbon disulphide, and the new sulphide dissolved in aqueous sodium hydroxide and reprecipitated by acids, which dissolve it when present in excess. This sulphide is also produced by passing hydrogen sulphide into a methyl-alcoholic solution of *p*-aminophenylarsenious oxide.

*p*-Acetylaminophenylarsenic sesquisulphide,  $\text{O}(\text{NHAs}\cdot\text{C}_6\text{H}_4\text{As})_2\text{S}_3$ , white, lustrous needles, m. p.  $208^{\circ}$ , is produced by dissolving acetyl-*p*-aminophenylarsinic acid in 25% aqueous ammonia, saturating the solution with hydrogen sulphide, and precipitating with dilute hydrochloric acid.

*Phenylglycinearsenic disulphide*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsS}_2$ , yellowish-white powder, decomposing at  $142^{\circ}$ , is produced by saturating with hydrogen sulphide an aqueous solution of phenylglycine-*p*-arsinic acid.

G. T. M.

**Preparation of the Salts of the Mercury Derivatives of Fluorescein.** HERMANN PAULY and VIKTOR TRAUMANN (D.R.-P. 201903).—The sodium salt of dimercurifluorescein is produced by adding mercuric chloride to a solution of fluorescein in sodium hydroxide. The yellowish-red precipitate then obtained is dissolved in sodium carbonate, and the red sodium salt isolated by evaporating the solution.

The sodium salt of tetramercurifluorescein is similarly prepared by treating the foregoing dimercuri-derivative with more mercuric chloride in alkaline solutions. These mercuric derivatives of fluorescein have the property of giving very fast shades of red with fabrics mordanted with chromium, iron, uranium, nickel, cobalt, aluminium, and cerium.

G. T. M.

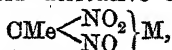
## Organic Chemistry.

**Formation of Mineral Oils from the Salts of Fatty Acids and the Metals of the Alkaline Earths.** A. KÜNKLER and H. SCHWEDHELM (*Seifensieder-Zeit.*, 1908, 35, 1285—1286, 1341—1342, 1365—1366, and 1393—1394).—Stearin was heated with calcium carbonate under pressure at varying temperatures in order to find out to what extent the decomposition of the resulting calcium stearate would lead to the formation of substances resembling the mineral oils. At 270° a decomposition sets in with the formation of solid products, and after eight hours' heating at 320° it is complete. The first decomposition products of calcium stearate and palmitate are paraffin wax, kerosene, and viscid oils. The products from calcium oleate are entirely liquid. The authors discuss the bearing of these experiments on the hypothesis that mineral oils are the products of the thermal decomposition of calcium and magnesium salts of the higher fatty acids derived from decaying animal matter. F. M. G. M.

**Optical and Certain other Properties of Grosny Naphtha.** MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 109).—The author has made an investigation, detailed results of which are to be given later, on the optical and other properties of all the distillation products of Grosny naphtha. The distillates having densities up to 8° on the saccharometer exhibit a dextro-rotation which increases with the sp. gr., colour, and viscosity. The viscosity and sp. gr. of the transparent distillates attain the values for castor oil, the fact that Grosny naphtha does not give lubricating oil depending on the different conditions employed in the works and in the laboratory, in which latter vacuum without steam is used. T. H. P.

**Optical Properties of Cheleken Ozokerite.** MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 109—110).—The author has investigated the products of Cheleken ozokerite distilling within the limits 130—280° at ordinary pressure. The solid distillates of a white to dark yellow colour dissolve to the extent of 2—5% in benzene or chloroform, the solutions exhibiting dextro-rotation. There is no doubt but that a genetic relation exists between ozokerite and naphtha. T. H. P.

**Coloured and Colourless Salts of Ethylnitrolic Acid.** ARTHUR HANTZSCH and GEORG KANASIRSKI (*Ber.*, 1909, 42, 889—893. Compare Graul and Hantzsch, *Abstr.*, 1899, i, 187).—Ethylnitrolic acid only absorbs generally in the ultra-violet, whereas its red alkali salts exhibit selective absorption; the acid is, therefore, a  $\psi$ -acid, and the red salt is a quinonoid derivative of the type



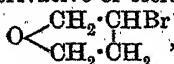
similar to those of the dinitro-paraffins (*Abstr.*, 1907, i, 500). The

colourless salts obtained from the coloured are much more stable, and, moreover, cannot be reconverted into the red isomerides. It has been found that the red potassium salt, when heated under petroleum at 45–50° in the light, is converted into the colourless; on a bright day the conversion is complete in one and a-half hours, on a dull day six hours are necessary. It is not decomposed at 110°, and molecular-weight determinations (1) in water, f. p. method, gave the ion number 2·2, 2·0, 2·1; (2) in methyl alcohol, b. p. method, 1·77 and 1·56, showing that the salt is unimolecular. Attempts to alkylate or acylate the colourless salt were without success, as also was an attempt to prepare the free acid. The dry potassium salt dissolved in xylene decomposes at 120° into methylcarbamide and potassium nitrite, and as its absorption in the ultra-violet is even less than that of the ethylnitrolic acid, the constitution  $\begin{matrix} \text{MeC:N} \\ \text{KO}\cdot\text{N}\cdot\text{O} \end{matrix} \text{>O}$  is assigned to this potassium ethyl isonitrolate (compare Wieland, this vol., i, 216). W. R.

**Allylcarbinol: Passage to the Furfuran Series.** H. PARISELLE (*Compt. rend.*, 1909, 148, 849–851).—The author gives a method for obtaining allylcarbinol in 20–25% yield from allyl bromide, trioxymethylene, and magnesium (compare Wagner, Abstr., 1894, i, 563; Carré, *Compt. rend.*, 1908, 146, 1283); diallyl and the formal of allylcarbinol,  $\text{CH}_2(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2)_2$ , b. p. 175–177°, are also formed.

$\gamma$ -Dibromobutyl alcohol,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , obtained by the action of bromine on allyl carbinol, has b. p. 112–114°/11 mm.: Wagner (*loc. cit.*) gave b. p. 131–141°/16 mm.

The action of potassium hydroxide on this bromide in ethereal solution yields the bromo-derivative of tetrahydrofuran,



b. p. 150–151°, which, when heated with powdered potassium hydroxide, yields dihydrofuran,  $\begin{matrix} & \text{CH}_2\cdot\text{CH} \\ & \diagdown \\ \text{O} & & \\ & \diagup \\ & \text{CH}_2\cdot\text{CH} \end{matrix}$  T. H. P.

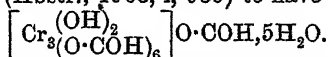
**The Lecithin of Egg-yolk.** HUGH MACLEAN (*Zeitsch. physiol. Chem.*, 1909, 59, 223–229).—Work on this phosphatide shows that some of the nitrogen is present in the form of choline, and part in some unknown form. Control experiments show that loss of choline during the analytical methods used will not account for the residual nitrogen. W. D. H.

**Lipoids of the Brain. I. Sphingomyelin.** OTTO ROSENHEIM and M. CHRISTINE TEBB (*Proc. physiol. Soc.*, 1909, li–liii; *J. Physiol.*, 38).—Sphingomyelin is the phosphorised constituent of so-called protagon, and may be separated from the non-phosphorised constituents of this mixture by combining fractional precipitation by means of acetone from alcohol-chloroform solutions with recrystallisation from pyridine. The term galactoside is adopted for the non-phosphorised substances just referred to.

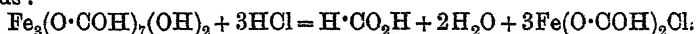
Sphingomyelin is a white, crystalline, non-hygroscopic substance which exhibits the phenomenon of sphæro-rotation previously described. It contains 4% of phosphorus, and the P : N ratio is 1 : 2 ; it is therefore a diamino-monophosphatide. On hydrolysis it yields choline and fatty acids, but not glycerol. On partial hydrolysis, it furnishes a substance which has some resemblance to the simplest nucleic acids, but this, on complete hydrolysis, yields phosphoric acid, a base, and a crystalline alcohol instead of a carbohydrate.

W. D. H.

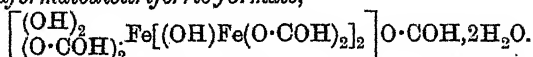
**Iron Formates.** E. BELLONI (*Arch. Pharm.*, 1909, 247, 123—130).—An investigation on the simple and complex formates of iron. The salt described by Scheurer-Kestner (*Ann. chim. phys.*, 1863, [iii], 68, 480) as a normal ferric formate, and when prepared by dissolving ferric hydroxide in formic acid, is shown to have the composition represented by the formula  $\text{Fe}_3(\text{O}\cdot\text{COH})_7(\text{OH})_2\cdot 4\text{H}_2\text{O}$ ; it is consequently analogous with the basic chromium formate which Werner has shown recently (*Abstr.*, 1908, i, 935) to have the formula



When the salt is treated with hydrochloric acid, it is decomposed, thus :



From this it follows that only one formyl group can function as an ion, and that two formyl groups are attached to each atom of iron; consequently, since the complex is univalent, eight of the nine valencies of the iron must be satisfied within the complex itself. Two of the four mols. of water are held very firmly, and are therefore situated in the complex; the compound is consequently a diaquo-salt, in agreement with which is the fact that the aqueous solution reacts acid. The conclusion is drawn, therefore, that the salt is probably *diaquohexaformatodioltriferric formate*,



It has not yet been found possible to replace the formyl group outside the complex by other acid radicles.

An aqueous solution of the salt when kept for some time exposed to the air deposits a brick-red precipitate, which is shown to be a *basic formate*,  $\text{Fe}(\text{OH})_2(\text{O}\cdot\text{COH})$ . The latter substance, when kept for about two months, has the composition  $\text{Fe}_3(\text{O}\cdot\text{COH})(\text{OH})_8$ .

The complex salts,  $\text{Fe}_3(\text{O}\cdot\text{COH})_4\text{Cl}_2\cdot 3\text{H}_2\text{O}$  (Scheurer-Kestner, *loc. cit.*),  $\text{Fe}(\text{O}\cdot\text{COH})_2\text{Cl}\cdot 1\frac{1}{2}\text{H}_2\text{O}$  (Rosenheim and Müller, *Abstr.*, 1904, i, 468), and  $\text{Fe}_2\text{Cl}_2(\text{O}\cdot\text{COH})_4\cdot \text{H}_2\text{O}$  (Benrath, *Abstr.*, 1905, i, 734), are shown to be identical with that prepared by the action of hydrochloric acid on hexaformatodioltriferric formate, which has the formula  $\text{Fe}(\text{O}\cdot\text{COH})_2\text{Cl}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ .

W. H. G.

**Sodium Acetates at 30°.** M. DUKELSKI (*Zeitsch. anorg. Chem.*, 1909, 62, 114—117).—An investigation of the phase-equilibrium of mixtures of sodium hydroxide, water, and acetic acid, or anhydride,

shows that the compounds capable of existence in the solid form at 30° are:  $C_2H_3O_2Na, \frac{1}{2}H_2O$ ,  $C_2H_3O_2Na, 3H_2O$ ,  $C_2H_3O_2Na, C_2H_4O_2$ , and  $C_2H_3O_2Na, 2C_2H_4O_2$ .

The results are expressed in a triangular diagram.

C. H. D.

**Glycerides of Fatty Acids. II. Occurrence of the Mixed Glycerides of Palmitic and Stearic Acids in Mutton Tallow.** ALOIS BÖMER [and, in part, G. HEIMSOETH] (*Zeitsch. Nahr. Genussm.*, 1909, 17, 353—396. Compare Abstr., 1907, i, 820).—It is shown that dipalmitylstearin and distearylpalmitin are present in the mixture of glycerides of saturated fatty acids occurring in mutton tallow; the separation of the various glycerides from one another is extremely difficult, and is only attained by repeated fractional crystallisation. No proof could be obtained of the presence of tripalmitin in the fat. The quantity of dipalmitylstearin, m. p. 57·5°, and distearylpalmitin, m. p. 63·6°, present in the mutton tallow examined was from 4 to 5%.

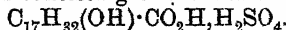
W. P. S.

**Crotonic Anhydride.** ANDREAS LUNIAK (*Ber.*, 1909, 42, 915—916).—*Crotonic anhydride*,  $(CHMe:CH:CO)_2O$ , is obtained in 80% yield when dry sodium crotonate is heated with crotonyl chloride (b. p. 34—36°/18 mm.,  $D^{20}_D$  1·0905: Henry gives  $D^{16}_D$  1·295, Abstr., 1899, i, 257) for three hours, and subsequently during eight hours after addition of ether. It is a colourless liquid, b. p. 113·5—114·5°/12 mm., 246—248°/766 mm.,  $D^{20}_D$  1·0397,  $n^{20}_D$  1·47446.

W. R.

**Essential Constituent of Turkey-red Oil and its Derivatives.** ADOLF GRÜN and M. WOLDENBERG (*J. Amer. Chem. Soc.*, 1909, 31, 490—506).—Turkey-red oil, obtained by the action of strong sulphuric acid on castor oil, consists essentially of a mixture of ricinoleic acid and its derivatives. The present paper contains an account of experiments carried out with the object of elucidating the course of the reaction between ricinoleic acid and sulphuric acid, and is a continuation of previous work (Grün, Abstr., 1907, i, 111; Grün and Wetterkamp, Abstr., 1908, i, 8).

When sulphuric acid is added gradually to ricinoleic acid at 0°, a clear liquid is obtained consisting of the additive compound,

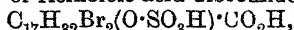


If the product is left for some time,  $\theta\lambda$ -dihydroxystearic acid, ricinoleic ricinoleate, ricinoleic lactide, and a small amount of ricinoleic acid sulphuric ester are produced. Attempts were made to prepare the sulphuric ester of methyl ricinoleate by the action of sulphuric acid and of chlorosulphonic acid on the methyl ester, but in each case the resulting product was chiefly the sulphuric ester of the acid itself. Ricinoleic acid sulphuric ester can be prepared by treating ricinoleic acid with an ethereal solution of chlorosulphonic acid at -5°. The compound is very stable towards alkali hydroxide at the ordinary temperature, but when boiled with water for four hours yields a product consisting of ricinoleic acid (38%) and the lactide (62%).

By the action of chlorosulphonic acid on ricinostearoleic acid (Ulrich, *Zeitsch. Chem.*, 1867, 3, 545), the sulphuric ester,

$\text{Me} \cdot [\text{CH}_2]_{15} \cdot \text{CH}(\text{O} \cdot \text{SO}_3\text{H}) \cdot \text{CH}_2 \cdot \text{C} : \text{C} \cdot [\text{CH}_2]_{17} \cdot \text{CO}_2\text{H}$ , is obtained as a clear, yellowish-brown oil; its *barium* salt forms a light yellow powder.

The sulphuric ester of ricinoleic acid dibromide,



obtained as a clear brown liquid by the action of chlorosulphonic acid on the dibromide, is decomposed by water. An attempt to prepare the sulphuric ester of methyl ricinoleate dibromide resulted in the production of the ester of the dibromide of the acid itself.

*Methyl λ-hydroxystearate*,  $\text{Me} \cdot [\text{CH}_2]_{15} \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_{10} \cdot \text{CO}_2\text{Me}$ , m. p. 58°, obtained by reduction of methyl ricinoleate, crystallises in white, silky plates. *λ-Hydroxystearic acid*, m. p. 78°, forms minute, white crystals; its sulphuric ester, m. p. 71–73°, is very stable, and is not decomposed by hot water.

By the action of phosphoric oxide on ricinoleic acid, two amorphous *polymerides* have been obtained, one of which is soluble in ether and is converted into potassium ricinoleate when heated with alcoholic potassium hydroxide, whilst the other is of a rubber-like consistence, is insoluble in all organic solvents, and cannot be reconverted into ricinoleic acid.

E. G.

**Preparation of Glyoxylic Acid as a Reagent.** STANLEY R. BENEDICT (*J. Biol. Chem.*, 1909, 6, 51–52).—A method is described for the preparation of glyoxylic acid from magnesium and oxalic acid. The magnesium salt of glyoxylic acid so obtained gives the reactions well in testing for tryptophan.

W. D. H.

**Citric Acid Fermentation.** REGINALD O. HERZOG and A. POLOTZKY (*Zeitsch. physiol. Chem.*, 1909, 59, (2), 125–128).—The authors find that the amount of citric acid formed depends very much on the nature of the sugar supplied. Lactose yielded very little, sucrose much more, and maltose still more. Xylose was more effective than arabinose. Erythritol gave no citric acid, and mannitol only little; notable quantities, however, were obtained from dextrose, mannose, laevulose, and glycerol. Further investigation is needed of this formation of citric acid from glycerol. The authors, unlike Mazé and Perrier, did not obtain citric acid from ethyl alcohol.

E. J. R.

**Humus Substances.** RUDOLF MIKLAUZ (*Chem. Zentr.*, 1909, i, 937–938; from *Zeitschr. Moorkult. Torfverwert.*, 1908, 285–327).—The action of mineral acids on peat is less the more completely the peat is humified. Humic acids from peat are altered by prolonged boiling with acids, the percentages of carbon and hydrogen increasing and diminishing respectively. Attempts to obtain pure substances by means of dilute alkali failed.

Dopplerte differs from peat in being much more strongly acid; the humic acid obtained from it by means of alkali does not, however, appreciably differ from that obtained from peat.

N. H. J. M.

**Ester-Acids of Thiocarboxylic Acids with Aliphatic Alcohol-Acids.** III. BROR HOLMBERG (*J. pr. Chem.*, 1909, [ii], 79, 253—270. Compare Abstr., 1907, i, 283).—The paper gives an account of the three acids which are theoretically obtained from carbamylglycollic acid by replacing the oxygen by sulphur. Of these three acids, carbamylthioglycollic acid,  $\text{NH}_2\cdot\text{CO}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , thiocarbamylglycollic acid,  $\text{NH}_2\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and thiocarbamylthioglycollic acid,  $\text{NH}_2\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , the first has long been known. It can be readily obtained by the interaction of aqueous sodium chloroacetate and solid ammonium thiocarbamate and subsequent acidification; so prepared, it has m. p.  $139-139.5^\circ$  (decomp.), and a  $K$  value 0.0266 by the conductivity method, and 0.0261 calculated from the rate of decomposition of ethyl diazoacetate, both values being greater than Ostwald's value, 0.0246. Thiocarbamylglycollic acid, prepared as previously described (*loc. cit.*), has m. p.  $111-112^\circ$ , and  $K$  value 0.113 and 0.108 by the preceding methods; the ammonium, sodium, and barium salts are mentioned. The anhydride,  $\text{NH}\begin{smallmatrix} \text{CS}\cdot\text{O} \\ \diagup \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$ , m. p.  $143^\circ$  (decomp.), is deposited by the evaporation of a warm solution of the acid in acetic anhydride, and has weak acid properties. When warmed with an equal weight of bromoacetic acid on the water-bath, thiocarbamylglycollic acid is changed into the isomeric carbamylthioglycollic acid.

**Thiocarbamylthioglycollic acid**,  $\text{NH}_2\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is obtained almost quantitatively by the interaction of a concentrated aqueous solution of sodium chloroacetate and solid ammonium dithiocarbamate and subsequent acidification. Owing to its tendency to yield the anhydride, the acid must be rapidly filtered and purified by the precipitation of its solution in acetone with chloroform. It darkens at  $100^\circ$ , has m. p.  $136-137^\circ$ , resolidifies, and then melts at  $168-169^\circ$  (decomp.), the m. p. of the anhydride; the sodium, calcium, lead, and barium salts are described. Thiocarbamylthioglycollic acid is very unstable, yielding thioglycollic and thiocyanic acids in alkaline solution, and its anhydride, rhodanin (rhodanic acid), in acid solution; even in neutral solution a slow decomposition into these three substances occurs. The ready formation of rhodanin from the acid is contributory evidence for the correctness of the constitution,  $\text{NH}\begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \diagup \\ \text{CS}\cdot\text{S} \end{smallmatrix}$ , ascribed by Liebermann and others to this substance.

**Trithiocarbodiglycollamide**,  $\text{CS}(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$ , prepared from potassium trithiocarbonate and chloroacetamide, or from ethyl trithiodiglycollate and cold concentrated ammonium hydroxide, forms glistening, yellow leaflets from water, and begins to decompose at  $195^\circ$ , but is not melted at  $205^\circ$ ; the aniline salt,  $\text{CS}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}, \text{PhNH}_2)_2$ , prepared from the acid and aniline in slightly warmed acetone, forms yellow needles, m. p.  $119-119.5^\circ$  (decomp.). C. S.

**Catalytic Preparation of Ketones.** JEAN B. SENDERENS (*Compt. rend.*, 1909, 148, 927—929. Compare Abstr., 1908, i, 494, 495; this vol., i, 127).—The [author continues his study of the catalytic

action of heated alumina on primary alcohols and aliphatic acids. Under the conditions described previously, methyl ether is obtained in good yield from methyl alcohol at 250—370°. Propyl alcohol in presence of heated alumina forms an ethylenic hydrocarbon and only 30% of propyl ether. *iso*Butyl alcohol forms *diisobutylene*. The use of other catalysts did not increase the yield of ether in the last two cases.

When the vapour of acetic anhydride is passed over alumina at 300—380°, acetone and carbon dioxide are obtained. The preparation of acetone from acetic acid has already been described. The higher ketones are more conveniently obtained, in a state of purity and with good yields, when anhydrous thorium dioxide is used as the catalyst. The following ketones have been prepared from the free acids at about 400°; diethyl ketone, dipropyl ketone, and *diisopropyl* ketone. Formic acid yields carbon dioxide and formaldehyde in presence of thorium dioxide at 200—250°. W. O. W.

**Transformation of Non-cyclic Diketones into Cyclic Compounds.** EDMOND É. BLAISE and A. KÖHLER (*Compt. rend.*, 1909, 148, 852—854).—The authors have investigated 1:6-, 1:7-, and 1:8-diketones in order to ascertain up to which term in the series diketones are convertible into cyclic compounds.

1:6-Diketones are readily transformed into cyclic derivatives by the action of alkali in boiling alcoholic solution. Contrary to the statement made by Perkin and Marshall (*Trans.*, 1890, 57, 241), octane- $\beta\eta$ -dione and its homologues yield practically pure 2-acidyl-1-alkyl- $\Delta^1$ -cyclopentenes,  $\text{CR} \begin{array}{c} \text{C}(\text{CO}\cdot\text{R}')\cdot\text{CH}_2 \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$ , under these conditions.

2-Propionyl-1-ethyl- $\Delta^1$ -cyclopentene,  $\text{CEt} \begin{array}{c} \text{C}(\text{COEt})\cdot\text{CH}_2 \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$ , prepared from decane- $\gamma\theta$ -dione, is a colourless liquid, b. p. 94—95°/14 mm., with an odour resembling that of camphor, and forms a *semicarbazone*, m. p. 188°, and an *oxime*, b. p. 127°/9 mm. When oxidised by means of permanganate, 2-propionyl-1-ethyl- $\Delta^1$ -cyclopentene yields propionic and  $\gamma$ -propionylbutyric acids.

Nonane- $\beta\theta$ -dione is converted into 2-acetyl-1-methyl- $\Delta^1$ -cyclohexene by cold concentrated sulphuric acid, but not by alkali (compare Perkin and Kipping, *Trans.*, 1890, 57, 13; 1891, 59, 214). Undecane- $\gamma\iota$ -dione, on the other hand, is not converted into a cyclic compound by sulphuric acid.

With 1:6-diketones, then, this transformation occurs readily, and does not appear to be influenced by the weight of the alkyl radicles attached to the carbonyl groups. But with 1:7-diketones, the change takes place less easily, and depends on the alkyl radicles united to the carbonyl groups.

Decane- $\beta\iota$ -dione is not converted into a cyclic compound either by alkali or by sulphuric acid. T. H. P.

**New Method for Determining the Constitution of Sugars.** MAURICE HANRIOT (*Compt. rend.*, 1909, 148, 640—643. Compare this vol., i, 206).—The aldopentoses and aldohexoses can be classified in

four groups according to the configuration of the substituents of the three carbon atoms adjacent to the CHO group. Since the isomerism of the chloralic acids depends only on the configuration of these three carbon atoms, it follows that the sugars of each group must give the same chloralic acid. This has been verified for the three groups of which dextrose, galactose, and mannose respectively are examples.

To determine the partial constitution of a sugar, it is converted into its chloralose; if this cannot be identified, it is oxidised to the corresponding chloralic acid; if this is not identical with any of the acids already described, the sugar must belong to the group of which talose and ribose are examples. Lævulose reacts with chloral to form a *chloralose*,  $C_8H_{11}O_6Cl_3$ , m. p. 228°. On oxidation this furnishes an acid,  $O < \begin{array}{c} \text{CH} \cdot \text{C}(\text{OH})(\text{CO}_2\text{H}) \cdot \text{CH} \cdot \text{CCl}_3 \\ \text{CH} \cdot \text{C}(\text{OH})(\text{CO}_2\text{H}) \cdot \text{O} \end{array}$ . This has m. p. 200—210°, and is very unstable. Attempts to prepare a chloralose from sorbose have been unsuccessful. W. O. W.

**$\beta$ -Hydroxy- $\delta$ -methylfurfuraldehyde as the Cause of Some Colour Reactions of Hexoses.** WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 217—226).—On dry distillation, or on heating with dilute acids, hexoses lose 3 molecules of water, yielding  $\beta$ -hydroxy- $\delta$ -methylfurfuraldehyde, the proportion obtained from ketoses being much higher than that from aldoses. The behaviour of this substance being similar to that of furfuraldehyde, it has frequently been mistaken for that compound. On its formation depend the test of Fiehe for artificial honey (*Zeitsch. Nahr. Genussm.*, 1908, 16, 75), Seliwanoff's reaction (*Abstr.*, 1887, 459), and Baudouin's sesamé oil reaction (*Villavecchia and Fabris, Abstr.*, 1893, ii, 197; 1894, ii, 126; 1898, i, 445). It also plays an important part in the reactions of Molisch (*Abstr.*, 1886, 923) and Udranszky (*Abstr.*, 1888, 863, 878, and 1889, 449). A. J. W.

**Styracitol.** Y. ASAHINA (*Arch. Pharm.*, 1909, 247, 157—160).—The formation of  $\beta$ -hexyl iodide from styracitol (*Abstr.*, 1908, ii, 59) and the preparation of a tetrabenzoate and tetranitrate of this compound show that it is an anhydrohexitol,  $C_6H_5O(\text{OH})_4$ . The optical rotatory power of styracitol given previously (*loc. cit.*) is incorrect; it should be  $[\alpha]_D^{25} - 56.47^\circ$  (1.0095 grams in 50 grams of water). The *tetrabenzoate*,  $C_6H_5O(\text{OBz})_4$ , crystallises in white, glistening leaflets, m. p. 142°,  $[\alpha]_D^{17} - 150.42^\circ$  (0.604 gram in 37.2 grams of chloroform). The *tetranitrate*,  $C_6H_5O(\text{O} \cdot \text{NO}_2)_4$ , prepared by adding styracitol to a mixture of concentrated sulphuric acid and fuming nitric acid, crystallises in white, glistening needles, m. p. 106°,  $[\alpha]_D^{17} - 31.82^\circ$  (0.654 gram in 20.025 grams of acetone). Styracitol is converted by concentrated sulphuric acid into *styracitoldisulphuric acid*; the barium salt,  $C_6H_{10}O_5(\text{SO}_3)_2\text{Ba}$ , is a white powder. As yet, only oxalic acid has been obtained by oxidising styracitol with 50% nitric acid. W. H. G.

**Mechanism of the Oxidation of Dextrose by Bromine in Neutral and Acid Solutions.** H. H. BUNZEL and ALBERT P. MATHEWS (*J. Amer. Chem. Soc.*, 1909, 31, 464—479).—Dextrose has both weakly basic and weakly acidic properties. A neutral or acid solution contains non-dissociated molecules,  $C_6H_{12}O_6$ , the free base,  $C_6H_{12}O_6, H_2O$ , and the ions  $C_6\bar{H}_{11}O_6$  and  $C_6\bar{H}_{13}O_6^+$ . These are formed according to the following reactions: (1)  $C_6H_{12}O_6 \rightleftharpoons C_6\bar{H}_{11}O_6 + H^+$  (2)  $C_6H_{12}O_6 + HCl \rightleftharpoons C_6\bar{H}_{13}O_6^+ + Cl^-$ , and (3)  $C_6H_{12}O_6 + H_2O \rightleftharpoons C_6H_{12}O_6, H_2O$ .

The object of the present investigation was to ascertain which of these components is most readily oxidised by bromine. The velocity of oxidation of dextrose has been determined in solutions containing varying quantities of hydrobromic, hydrochloric, sulphuric, and phosphoric acids up to a concentration of 0.5*N*, both in the presence and absence of sodium bromide. The determinations were made by measuring the rate of disappearance of the bromine.

It has been found that the course of the oxidation in presence of an excess of dextrose is represented quantitatively by the equation  $dx/dt = a(A - x)[K^v + K_4/(B + 2x)^2]$ , in which  $a(A - x)$  is the concentration of the active bromine,  $(B + 2x)$  the concentration of the hydrogen ions, and  $K^v$  and  $K_4$  the constants of two reactions. All the results of the experiments agree quantitatively with the hypothesis that dextrose undergoes ionisation in aqueous solution to form the ions  $C_6\bar{H}_{11}O_6$  and  $C_6\bar{H}_{13}O_6^+$ , and that these ions are the particles actually oxidised by the bromine. The oxidation of dextrose by bromine in neutral or acid solution yields a large proportion of gluconic acid. Since the solution, even if neutral at first, rapidly becomes acid owing to the formation of hydrobromic acid, the reaction of the  $-$  ion will be quickly suppressed and the oxidation of the  $+$  ion only will take place. Hence it is evident that the oxidation of the  $+$  ion results in the formation of gluconic acid. In view of the large amount of gluconic acid obtained by Nef (*Abstr.*, 1908, i, 7) in the oxidation of dextrose by Fehling's solution, it seems probable that gluconic acid is also derived from some other source than the  $+$  ion, but whether from the  $-$  ion or from the non-dissociated molecule cannot be definitely stated.

E. G.

**Spontaneous Oxidation of Sugars.** ALBERT P. MATHEWS. **Spontaneous Oxidation of Cysteine.** ALBERT P. MATHEWS and SYDNEY WALKER. **Action of Cyanides and Nitriles on the Spontaneous Oxidation of Cysteine.** ALBERT P. MATHEWS and SYDNEY WALKER (*J. Biol. Chem.*, 1909, 6, 3—20, 21—23, 29—38).—Lævulose, galactose, dextrose, maltose, and lactose oxidise rapidly in the air in alkaline solutions. This shows that for oxidation it is necessary to form a salt of the sugar, which ionises, and the resulting disturbance of electrical equilibrium in the anion causes its easy oxidation: Lævulose oxidises most rapidly; the other sugars oxidise at about an equal speed, approximately one-quarter that of lævulose.

In the body, oxydases are believed to include (1) activators of oxygen, and (2) activators of the reducing substances by dissociation; the latter, which are more important, are specific, the former not: Cysteine is rapidly oxidised to cystine in neutral media, that is, about the reaction of blood. Cyanides and most nitriles check or hinder this action, probably by uniting with the sulphur group which the oxygen ordinarily attacks. This suggests a similar action of these poisons on cellular respiration.

W. D. H.

**Conjugated Phosphoric Acids of Plant Seeds.** PHEBUS A. LEVENE (*Biochem. Zeitsch.*, 1909, 16, 399—405).—Phytin consists partly of a condensation product of inosite with phosphoric acid (compare Neuberg, Abstr., 1908, i, 394), but partly, also, of a condensation product of phosphoric acid with glycuronic acid. A complete separation of the two constituents was not possible (compare following abstract).

G. B.

**Phytin.** CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 16, 406—410. Compare Abstr., 1908, i, 394; Levene, preceding abstract).—Mainly polemical. Neuberg has shown that phytin is inosite-phosphoric acid; Levene claims to have resolved it into this substance and into glycuronic acid-phosphoric acid. Eight different phytin preparations are now found to give no-glycuronic acid reaction.

E. F. A.

**Cellulose Hydrates.** CHARLES F. CROSS and EDWARD J. BEVAN (*Chem. Zeit.*, 1909, 33, 368).—Polemical. A reply to Ost and Westhoff (this vol., i, 210).

L. DE K.

**Preparation of Esters of Cellulose and their Transformation Products by the Action of Acid Anhydrides in the Presence of Salts.** KNOLL & Co. (D.R.-P. 206950).—Other acid anhydrides besides acetic anhydride condense with cellulose to form various stable esters. *Propionylcellulose* is produced by dissolving cotton wool in a mixture of propionic anhydride and glacial acetic acid containing a small proportion of ammonium sulphate. A butyryl ester is similarly obtained by dissolving cellulose or hydrocellulose at 70° in a mixture of butyric anhydride and glacial acetic acid containing methylamine sulphate.

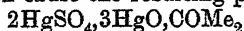
F. M. G. M.

**Formation of Hydrocelluloses by means of Sulphuric Acid.** GEORG BÜTTNER and J. NEUMANN (*Zeitsch. angew. Chem.*, 1909, 22, 585. Compare this vol., i, 86).—A reply to Schwalbe (*ibid.*, 136). The importance and usefulness of analytical data for hydrocelluloses are emphasised.

J. J. S.

**Distillation of Wood with Superheated Steam.** GEORG BÜTTNER and HANS WISLICENUS (*J. pr. Chem.*, 1909, [ii], 79, 177—234).—A systematic investigation of the destructive distillation of wood has not been undertaken since Violette's original researches. The present paper deals with the dry distillation, and the distillation with superheated steam, of cellulose and of wood, on the small and on the large

scale, and with the estimation of the products. Concordant determinations of the acetic acid, methyl alcohol, ketones, and reducing agents in the crude pyroligneous acid can be obtained only by suitable preliminary treatment of the crude distillate. The acetic acid is estimated by treating the crude aqueous distillate with dilute sulphuric acid, distilling with steam, and titrating the distillate with *N*/10-sodium hydroxide and phenolphthalein, volatile acids other than acetic being present in negligibly small amount. The methyl alcohol and the ketones (calculated as acetone) are estimated by filtering a measured volume of the crude distillate, neutralising with solid sodium carbonate, again filtering, making the filtrate strongly alkaline, and distilling, the first half of the distillate being shaken with animal charcoal, filtered, and made up to volume; in one portion of this solution the methyl alcohol is determined by Zeisel's method, whilst in another portion the ketones are estimated by Denigès' mercuric sulphate method, after preliminary treatment with hydrogen peroxide to destroy impurities which cause the resulting precipitate,



(dried at  $90^\circ$ ), to be coloured. The reducing agents are estimated by warming the crude distillate with ammoniacal *N*/10-silver nitrate, and determining, after filtration, the excess of silver nitrate by ammonium thiocyanate. The water, coke, and tar are determined by direct weighing; and the gaseous constituents are measured at the ordinary temperature and pressure. All %'s are calculated on cellulose or wood dried at  $120^\circ$ .

Preliminary experiments were performed on cellulose (filter paper), which was subjected to dry distillation in an iron tube heated to a dark red heat in an ordinary gas furnace, the volatile products passing through a condenser and being collected in two receivers and a gas-holder. Analysis of the products gives (on 41.62 grams of cellulose) 20.07% charcoal, 5.97% tar, 2.76% acetic acid, 0.04% ketones, and 7.56% reducing agents, the outstanding feature being the absence of methyl alcohol. In the next experiment the tube was heated in a Heraeus electrical resistance furnace to ensure more equable heating; the distillation occurred between  $140^\circ$  and  $470^\circ$ , and the results were very similar to the preceding, the chief difference being an increase of 10% in the amount of charcoal. Again, methyl alcohol is not produced. In another experiment with the electric furnace, the temperature was raised to  $140^\circ$ , when steam at  $125^\circ$  was admitted, and the distillation continued up to  $460^\circ$ . Methyl alcohol is not formed, the % of reducing agents is doubled, and the charcoal decreases 7.5%. Next, with the same apparatus, the temperature was raised to  $150^\circ$ , steam at  $140^\circ$  admitted, and the distillation continued up to a very high, unmeasured temperature; the cellulose is completely destroyed, no charcoal, tar, or methyl alcohol is formed, only a trace of ketone, 1.7% acetic acid, and 5.18% reducing agents being produced, apart from gaseous products.

Similar experiments on wood have been performed on the small scale. The iron tube, packed with beech wood or hornbeam, was heated to  $150^\circ$  in the electric furnace, steam at  $140^\circ$  admitted, and the distillation continued up to  $350^\circ$ . The %'s are as follows: charcoal

35.1, tar 4.30, acetic acid 10.30, methyl alcohol 0.27, ketones 0.41, and reducing agents 8.49. A comparative examination of the products of the distillation of cellulose and of wood shows that the formation of acetic acid is largely, and of methyl alcohol is entirely, due to the lignin of the wood.

The rapid distillation of beech wood with steam at 350—425° leads to an increase in the amount of gas, tar, and reducing agents, the % of acetic acid being unchanged. This result is important, because dry distillation, as ordinarily practised, must proceed slowly in order to avoid a decrease in the amount of acetic acid formed.

In these experiments with superheated steam, the aqueous distillate is necessarily very dilute. It is shown, however, that the decomposition of wood by steam begins at 240°, and that all the valuable products come over in the fraction between 240—300°; the carbonisation of the wood can then be completed at a higher temperature without any valuable product collecting in the distillate.

Attempts have been made to increase the yield of acetic acid by the oxidation of the reducing agents (mainly acetaldehyde) formed in the distillation. Distillation of wood with a mixture of air and superheated steam is of no use, as also is the passing of air through the crude acetic acid. The addition of hydrogen peroxide, however, to the crude aqueous distillate (containing 8% of acetic acid and 7.53% of reducing agents) and distillation with a few c.c. of dilute sulphuric acid yields a distillate containing 18.86% of acetic acid.

The experience gained in these experiments has been applied on a manufacturing scale. A description and sections of the plant are given, but the results are disappointing; for example, in an experiment on 15,800 grams of beech wood, the yield of acetic acid is only 3.34%, whilst the amounts of methyl alcohol, reducing agents, and ketones are 0.24, 2.64, and 0.19% respectively.

It has been noticed that, whilst the average temperature of the retort is about 300°, the escaping gases and vapours have a temperature of 400—500°, proving that an exothermic reaction must occur among the products of the distillation of wood with superheated steam.

C. S.

**New General Method for Preparation of Aliphatic Amines.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1909, 148, 898—901. Compare *Abstr.*, 1908, i, 594, 713).—In the presence of heated thorium dioxide or tungsten trioxide, primary alcohols react readily with ammonia to form water and a primary amine without the formation of an ethylenic hydrocarbon. Under the same conditions, alcohols react with primary amines to give secondary and tertiary amines. This observation has led to the discovery of a method for preparing aliphatic amines which is more convenient than Merz's method (*Abstr.*, 1884, 984). The alcohol vapour and dry ammonia, or the vapour of a primary amine, are passed over a few grams of the catalyst at 350—370°. The product condenses to a liquid containing a primary and secondary amine with a small quantity of the tertiary amine and also water, ammonia, and unaltered alcohol; the latter is removed by distillation. The following amines have been prepared in

this way: *iso*Amylamine, *diiso*amylamine, *ethyliso*amylamine, *propyliso*amylamine,  $\text{Pr}^a(\text{C}_5\text{H}_{11})\text{NH}$ , b. p.  $141^\circ$ , *isobutyliso*amylamine,  $\text{C}_9\text{H}_{21}\text{N}$ , b. p.  $158-160^\circ$ .

The application of the method to aromatic, secondary, and cyclic alcohols will form the subject of a further communication.

W. O. W.

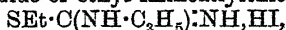
**Homologues of Arginine.** ERNST WINTERSTEIN and ALBERT KÜNG (*Zeitsch. physiol. Chem.*, 1909, 59, 141—164).—Thiocarbamide, by shaking with mercuric oxide in ethereal suspension, passes largely into the condition of cyanamide. By heating  $\alpha\beta$ -dibromopropionic acid with ammonia and ammonium carbonate, *isoserine* is obtained, and not  $\alpha\beta$ -diaminopropionic acid as expected. By the action of  $\alpha\beta$ -dibromopropionic acid on guanidine carbonate, an amorphous, nitrogenous substance is obtained in addition to guanidine hydrobromide. By the condensation of cyanamide with  $\alpha\beta$ -diaminopropionic acid, a lower homologue of arginine is formed, namely,  *$\alpha$ -amino- $\beta$ -guanidinepropionic acid*. The *hydrochloride*,



forms colourless, transparent, monoclinic (?) prisms, decomp.  $180-181^\circ$ ; the *picrate* crystallises in slender needles, decomp.  $200^\circ$ . After the reaction between lysine and cyanamide, no higher homologues of arginine could be separated out.

W. D. H.

**Thiodine.** ROGER DOURIS (*Bull. Sci. Pharmacol.*, 1908, 15, 629—631).—This drug is prepared by heating equimolecular proportions of thiosinamine (allylthiocarbamide) and ethyl iodide in a reflux apparatus. Contrary to the supposition of its discoverer, Weiss, the ethyl group in thiodine is attached to the sulphur atom, for, on oxidation, ethanesulphonic acid is formed. Thiodine is therefore either the hydriodide of ethyl iminoallylthiocarbamate,



or of ethyl allyliminothiocarbamate,  $\text{SEt} \cdot \text{C}(\text{NH}_2, \text{HI}) : \text{N} \cdot \text{C}_3\text{H}_5$ . The substance forms colourless crystals, m. p.  $69^\circ$ ; the corresponding hydrochloride is crystalline and very hygroscopic. The *picrate* has m. p.  $123^\circ$ .

G. B.

**Oxidation of Glutamic and Aspartic Acids by Hydrogen Peroxide.** HENRY D. DAKIN (*J. Biol. Chem.*, 1909, 5, 409—412).—Glutamic acid (like monoaminomonocarboxylic acids) is readily oxidised when the ammonium salt is warmed with hydrogen peroxide, with the liberation of ammonia, carbon dioxide, and formation of succinic acid. A similar reaction is brought about by yeast (Ehrlich) and putrefactive organisms. With aspartic acid, essentially the same reaction occurs, but the change is complicated by the fact that the primary product of the reaction, namely, the semialdehyde of malonic acid, is very unstable and breaks up easily into acetaldehyde and carbon dioxide.

W. D. H.

**Cyanohydrins.** A. J. ULTEE (*Rec. trav. chim.*, 1909, 28, 1—23).—Lapworth (*Trans.*, 1903, 83, 995) has shown that the addition of hydrogen cyanide to aldehydes and ketones is accelerated by an

alkaline catalyst, but, hitherto, attempts to isolate the cyanohydrin formed by distillation of the reaction product have failed. The failure is due to the reversible action of the alkali regenerating the hydrogen cyanide and aldehyde or ketone. Accordingly, if after the reaction is completed the catalyst is neutralised by a trace of sulphuric acid, the cyanohydrin produced can be readily isolated by distilling the reaction mixture under reduced pressure. Utilising this fact, the author has prepared a number of cyanohydrins, some of which have been described previously, in a pure state, and determined their physical constants. Contrary to the generally accepted statement of Urech (*Annalen*, 1872, 164, 259), the cyanohydrins do not precipitate silver nitrate solution, and the amount of cyanohydrin present at the equilibrium condition, resulting when the latter is treated with a trace of alkali, has been determined for each compound by estimating the free hydrogen cyanide as silver cyanide. *α*-Hydroxyisobutyronitrile, which, although already described (compare Urech, *loc. cit.*; Tiemann and Friedländer, *Abstr.*, 1882, 56; Pinner, *Abstr.*, 1884, 1292; Henry, *Abstr.*, 1899, i, 182; Bucherer and Grolée, *Abstr.*, 1906, i, 405), has not hitherto been obtained pure, is a colourless, inodorous liquid, b. p. 82°/23 mm., m. p. -19°,  $D^{19}_D$  0.9320,  $n^{19}_D$  1.40002, which very largely dissociates when heated at 170—175°. At the condition of equilibrium, equimolecular quantities of acetone and hydrogen cyanide combine to the extent of 94.15% at 0°, 88.60% at 25°. *α*-Hydroxy-*α*-methylbutyronitrile is a liquid,  $D^{10}_D$  0.9303,  $n^{19}_D$  1.41525, which does not crystallise on cooling, but forms a hard, vitreous mass. In the equilibrium mixture, 95.57% of the cyanohydrin is present at 0°, 90.36% at 25°. *α*-Ethyl-*α*-hydroxybutyronitrile, a liquid, b. p. 97.5°/18.5 mm.,  $D^{18.5}_D$  0.9300,  $n^{19}_D$  1.42585, is the first of the series which is not completely miscible with water. At 0° addition takes place to the extent of 95.90%, and at 25° 91.29%. *α*-Hydroxy-*α*-methylvaleronitrile,  $\text{OH} \cdot \text{CMePr} \cdot \text{CN}$ , is a liquid, b. p. 100°/21 mm.,  $D^{18}_D$  0.9166,  $n^{19}_D$  1.42585, which is present in the equilibrium mixture to the amount of 93.87% at 0°, 88.08% at 25°. *α*-Hydroxy-*αβ*-dimethylbutyronitrile has b. p. 97°/19 mm.,  $D^{18}_D$  0.9334,  $n^{19}_D$  1.42755. The amount present at equilibrium is 95.88% at 0°, 91.32% at 25°. *α*-Hydroxy-*α*-methylhexonitrile,  $\text{CH}_2\text{Pr} \cdot \text{CMe}(\text{OH}) \cdot \text{CN}$ , is a liquid, b. p. 114°/21 mm.,  $D^{18.5}_D$  0.9102,  $n^{19}_D$  1.42915, of which 94.24% is present at equilibrium at 0°, 87.45% at 25°. *α*-Hydroxy-*αγ*-dimethylvaleronitrile,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CN}$ , a colourless, odourless liquid, b. p. 109°/24 mm.,  $D^{20}_D$  0.9047,  $n^{21}_D$  1.42595, is more readily dissociated, only 82.51% being present in equilibrium at 0°, and 69.84% at 25°. *α*-Hydroxy-*αβγ*-trimethylbutyronitrile could not be obtained pure; the substance recrystallised from light petroleum has m. p. 103—104°. Carlinfanti (*Abstr.*, 1898, i, 234) observed 82—87°. *α*-Hydroxy-*α*-propylvaleronitrile,  $\text{CPr} \cdot (\text{OH}) \cdot \text{CN}$ , which has b. p. 119°/21 mm.,  $D^{18}_D$  0.9077,  $n^{19}_D$  1.43366, is present in the equilibrium mixture to the extent of 92.88% at 0°, 84.81% at 25°. *β*-Chloro-*α*-hydroxy-*α*-methylpropionitrile (Bischoff, *Ber.*, 1872, 5, 865) is a liquid, b. p. 110°/22 mm.,  $D^{15}_D$  1.2027,  $n^{19}_D$  1.45362. The amount present in equilibrium at 0° is 97.75%, at 25° 94.94%. 1-Cyanocyclohexanol forms very hygroscopic crystals, m. p. 29°, b. p. 125.5—126°/17.5 mm. It is only slightly dissociated at 25°, the equilibrium mixture containing 98.61% of the

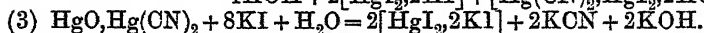
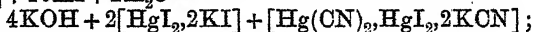
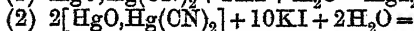
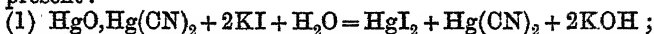
nitrile. The latter condenses with aniline, giving colourless needles of 1-anilinocyclohexanonitrile,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{NHPh}) \cdot \text{CN}$ , m. p. 73°.

Ethyl  $\alpha$ -cyano- $\alpha$ -hydroxypropionate (compare Gerson, Abstr., 1887, 260) is a colourless liquid, b. p. 105—105·5°/19 mm.,  $D_{16}^{20}$  1·0988,  $n_D^{20}$  1·42435, of which 98·17% is present in the equilibrium mixture at 25°. Ethyl  $\beta$ -cyano- $\beta$ -hydroxybutyrate is a colourless, odourless liquid, b. p. 127—128°/16·5 mm., m. p. 8·5°,  $D_{13}^{25}$  1·0886,  $n_D^{13.5}$  1·43557, which is more readily dissociated than the preceding compound, the equilibrium mixture at 0° containing 94·02%, and at 25° 87·71%, of the ester.

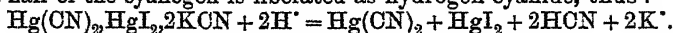
When ethyl lævulate containing a small quantity of potassium cyanide is treated with hydrogen cyanide and the product after remaining overnight distilled under reduced pressure, a solid, m. p. 29—30°, is obtained which seems to be identical with Tollens and Block-Kreckeler's cyanovalerolactone (Abstr., 1887, 800). All the above cyanohydrins with the exception of  $\beta$ -chloro- $\alpha$ -hydroxy- $\alpha$ -methylpropionitrile were analysed by hydrolysis with potassium hydroxide and estimation of the cyanide by titration with  $N/10$ -silver nitrate solution, this being found the most accurate method.

E. H.

**Mercuric Oxycyanide.** ERWIN RUPP and S. GOY (*Arch. Pharm.*, 1909, 247, 100—107. Compare Abstr., 1908, i, 770).—Mercuric oxycyanide when treated with potassium iodide behaves as a mixture of mercuric oxide and mercuric cyanide. The reaction proceeds in one of the following ways, depending on the proportion of potassium iodide present:



The complex salt,  $\text{Hg}(\text{CN})_2, \text{HgI}_2, 2\text{KCN}$ , crystallises in silky, white needles; its aqueous solution reacts acid towards litmus and neutral towards phenolphthalein. When the salt is acted on by an acid, only one-half of the cyanogen is liberated as hydrogen cyanide, thus:



In the presence of an excess of potassium iodide a state of equilibrium exists, represented by the equation:  $2[\text{HgI}_2, 2\text{KI}] + 4\text{KCN} \rightleftharpoons [\text{Hg}(\text{CN})_2, \text{HgI}_2, 2\text{KCN}] + 6\text{KI}$ . The complex cyanide separates when the solution is concentrated, although the aqueous solution is practically a solution of potassium cyanide and potassium mercuric iodide, as represented by the left-hand side of the equation. Mercuric oxycyanide also behaves as a mixture of mercuric oxide and mercuric cyanide towards iodine, hydrochloric acid, hydrobromic acid, and hydriodic acid.

W. H. G.

**Preparation of Aromatic Nitro-compounds.** CHEMISCHE FABRIK GRÜNAU LANDSHOFF & MEYER ATKIEN-GESELLSCHAFT (D.R.-P. 207170).—The nitrous fumes obtained by the electrical oxidation of atmospheric nitrogen are absorbed by a weak basic oxide, such as zinc or copper oxide, and the product when heated at 500° evolves again the oxides of nitrogen, from which nitric acid can be prepared.

When, however, a mixture of benzene and air is passed over the mixed zinc nitrite-nitrate at 300—350°, nitration of the hydrocarbon occurs, and pure nitrobenzene is produced in quantitative yield. At higher temperatures a decomposition sets in. The residual zinc oxide may be used in subsequent operations. Toluene, when nitrated by this method at about 400°, gives *m*-nitrotoluene (11%) and the para-isomeride (89%). In combination with Sabatier's reduction process, this method furnishes a means of preparing aniline directly and continuously from benzene compounds.

F. M. G. M.

**2:5- and 4:5-Dinitro-*m*-xylenes.** JAN J. BLANKSMA (*Rec. trav. chim.*, 1909, 28, 92—96).—It has been stated previously (Abstr., 1906, i, 11) that by nitrating *s*-nitro-*m*-xylene with nitric acid, D 1.52, 4:5-dinitro-*m*-xylene, m. p. 132°, is formed. The latter compound is also obtained by nitrating 5-nitroaceto-*m*-xylidide, removing the acetyl group by hydrolysis, and eliminating the amino-group by diazotisation. Since Klages (Abstr., 1896, i, 290) prepared the same compound, but regarded it as 2:5-dinitro-*m*-xylene, the present work was undertaken in order definitely to determine its constitution.

4:6-Dinitro-*m*-xylene on partial reduction gives 6-nitro-4-amino-*m*-xylene, which, when acetylated with a mixture of acetic anhydride and acid, gives 6-nitroaceto-*m*-xylidide, m. p. 160°. Nitration of the latter with nitric acid, D 1.52, or a mixture of nitric and sulphuric acids, gives 5:6-dinitroaceto-*m*-xylidide, m. p. 217°, identical with that prepared by nitrating 5-nitroaceto-*m*-xylidide. Elimination of the amino-group from 5:6-dinitro-*m*-xylidine, m. p. 120° (Klages gives 115°, and 226° for the acetyl derivative), by the diazo-reaction gives 4:5-dinitro-*m*-xylene, of which the constitution is therefore proved.

The 4:5-dinitro-*m*-xylene is transformed by nitration into 4:5:6-trinitro-*m*-xylene. A new proof of the constitution of the latter is furnished by transforming it into 4:6-dinitro-5-amino-*m*-xylene by heating with alcoholic ammonia and eliminating the amino-group, giving 4:6-dinitro-*m*-xylene.

2-Nitroaceto-*m*-xylidide, m. p. 147°, prepared by acetylating Noeltling, Braun, and Thesmar's 2-nitro-4-amino-*m*-xylene (Abstr., 1901, i, 588), on nitration with nitric acid, D 1.52, gives clear yellow crystals of 2:5-dinitroaceto-*m*-xylidide, m. p. 233°. The latter, on hydrolysis, gives 2:5-dinitro-*m*-xylidine, from which the amino-group is eliminated, giving 2:5-dinitro-*m*-xylene, colourless crystals, m. p. 101°, which become yellow on exposure to light. The constitution of the latter substance is proved by its transformation into 2:4:5-trinitro-*m*-xylene when nitrated.

Methods are described for the preparation of 2:5- and 4:5-dinitro-*m*-xylenes from *m*-xylene. The four possible isomeric dinitro-*m*-xylenes have now been described.

E. H.

**Benzeneselenonic Acid and Related Compounds.** HOWARD W. DOUGHTY (*Amer. Chem. J.*, 1909, 41, 326—337).—Benzene-selenonic acid,  $C_6H_5 \cdot SeO_3H$ , is formed when benzene and selenic acid are heated together on a water-bath or in a sealed tube at 110°. It has m. p. 142°, and gives off carbon dioxide and water when heated

at 180°. The barium salt crystallises from cold or warm solutions with  $3\text{H}_2\text{O}$ , from hot solutions with  $2\text{H}_2\text{O}$ .

*Phenyl silver selenide*,  $\text{SeAgPh}$ , is obtained as a yellow precipitate when a solution of benzeneselenonic acid is mixed with the equivalent quantity of silver nitrate and sulphur dioxide is then added.

Benzeneseleninic acid is precipitated when benzeneselenonic acid is treated with concentrated hydrochloric acid in the cold. It crystallises without water of crystallisation. When heated at 130°, it forms *benzeneseleninic anhydride*, m. p. 164°, subliming about 130°; the anhydride is not changed by heating at its melting point, but decomposes at 200°. It is very hygroscopic, and on exposure to the air it absorbs moisture, forming benzeneseleninic acid. H. M. D.

**New Method for the Preparation of  $\beta$ -Halogen Derivatives of Naphthalene** GEORGES DARZENS and ERNEST BERGER (*Compt. rend.*, 1909, 148, 787—788).—In addition to esters of phosphorous and phosphoric acids,  $\beta$ -halogen derivatives of naphthalene are obtained when the sodium derivative of  $\beta$ -naphthol is treated with a halogen or oxy-halogen derivative of phosphorus.

The best yield (55%) was obtained with phosphorus trichloride, which was dissolved in dry toluene and heated for an hour on the water-bath with the sodium derivative of  $\beta$ -naphthol suspended in the same solvent. The product was then treated with water and distilled in steam. W. O. W.

**Hydrogenation of Fluorene.** LEOPOLD SPIEGEL (*Ber.*, 1909, 42, 916—920. Compare Abstr., 1908, i, 331).—Polemical. A reply to Schmidt. The reduction product of fluorene is not a decahydro-fluorene, but the perhydride,  $\text{C}_{18}\text{H}_{22}$ , D<sup>22</sup> 0.9203, M<sub>D</sub> 55.66 (Abstr., 1908, i, 16; this vol., i, 19). W. R.

**Preparation of 3-Chloro-6-nitroaniline.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 206345).—3-Chloro-6-nitroaniline and its sulphonic acid, which are of importance in connexion with the production of azo-dyes, are now readily prepared by the following series of operations.

3-Chloroacetanilide is sulphonated with fuming acid (20%  $\text{SO}_3$ ) at the ordinary temperature, and the mixture then treated with mixed nitric and sulphuric acids at -5°. On pouring the nitration product into a large volume of water and warming at 70—80°, the acetyl group is removed, and the addition of potassium chloride leads to the formation of potassium 3-chloro-6-nitroaniline-4-sulphonate. This salt, which is only sparingly soluble in cold water, gives a yellow diazo-derivative. When boiled with 3.5 parts of sulphuric acid (55° Bé), the sulphonic group is eliminated, and 3-chloro-6-nitroaniline, m. p. 124—125°, is produced. F. M. G. M.

**Bromination of the Dinitroanilines.** JAN J. BLANKSMA (*Rec. trav. chim.*, 1909, 28, 97—104).—2:3-, 3:4-, and 3:6-Dinitroanilines were prepared according to the method described by Wender (Abstr., 1890, 884).

When 3:6-dinitroaniline, dissolved in glacial acetic acid, is heated with bromine (1 mol.) in a sealed tube on a water-bath, the product consists of 4-bromo-3:6-dinitroaniline, yellow crystals, m. p. 186°, which on similar treatment gives 2:4-dibromo-3:6-dinitroaniline, m. p. 140°. The constitution of the 4-bromo-3:6-dinitroaniline is proved by the production of the acetyl derivative, m. p. 152°, together with 4-bromo-2:3-dinitroacetanilide, m. p. 185°, by the nitration of 4-bromo-3-nitroacetanilide, prepared according to Noelting and Collin's method (Abstr., 1884, 1011).

The constitution of 4-bromo-2:3-dinitroacetanilide is established by the fact that the amine obtained by hydrolysis gives 4:6-dibromo-2:3-dinitroaniline, not 2:4:6-tribromo-3:5-dinitroaniline (Abstr., 1902, i, 600) when treated with excess of bromine.

2:3-Dinitroaniline, when brominated in a sealed tube, gives 6-bromo-2:3-dinitroaniline, deep red crystals, m. p. 158° (not 4-bromo-2:3-dinitroaniline, which has the same m. p.), which on further bromination gives 4:6-dibromo-2:3-dinitroaniline, m. p. 100°.

Bromination of 3:4-dinitroaniline under similar conditions gives clear yellow crystals of 6-bromo-3:4-dinitroaniline, m. p. 186°, which can be again brominated, giving 2:6-dibromo-3:4-dinitroaniline, yellow crystals, m. p. 201°.

6-Bromo-3-nitroaniline, prepared according to Wheeler's method (Abstr., 1896, i, 23), on acetylation gives colourless crystals of 6-bromo-3-nitroacetanilide, m. p. 183°, which when nitrated gives 6-bromo-3:4-dinitroacetanilide, colourless crystals, m. p. 165°. The latter on hydrolysis gives an amine identical with the 6-bromo-3:4-dinitroaniline obtained from 3:4-dinitroaniline, thus establishing the constitution of the former compound.

The author confirms the observation of Körner and Contardi (Abstr., 1908, i, 523) that bromination of 3:5-dinitroaniline gives 2-bromo-3:5-dinitroaniline. The latter, with excess of bromine, gives 2:4:6-tribromo-3:5-dinitroaniline.

All attempts to prepare 1:3-dibromo-2:5-dinitrobenzene, of which a small quantity is probably formed in the nitration of 1:3-dibromo-5-nitrobenzene, by eliminating the amino-group from 2:4-dibromo-3:6-dinitroaniline failed.

E. H.

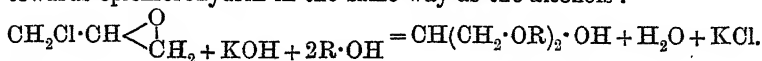
**Colouring and Dyeing Properties of Picric Acid.** LÉO VIGNON (*Compt. rend.*, 1909, 148, 844—846).—The intensity of colour of solutions of picric acid in water, alcohol, benzene, and ether varies in the same sense as the electrical conductivities of the solutions. Aqueous solutions of picric acid are able to dye wool, but only when their electrical conductivities exceed a certain minimum value, which may be attained either by a sufficient concentration of the picric acid or by the addition of a small proportion of an acid, such as hydrochloric, to solutions of lower concentrations. With alcoholic solutions of picric acid containing 1 part of hydrochloric acid per 10,000, the fixation of colouring matter by wool is very slight, in spite of a moderately high conductivity.

The fixation of picric acid by wool seems to be due to a chemical action between the fibre of the wool and the highly-ionised colouring

matter. This chemical action is apparently not a salt-forming phenomenon, since, although picric acid dissolved in benzene forms salts with organic bases (compare Abstr., 1908, ii, 664), such solutions have no dyeing action on wool.

T. H. P.

**Action of Potassium Hydroxide on Epichlorohydrin in Presence of Monohydric Phenols.** VIRGILIO ZUNINO (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 254—256. Compare Abstr., 1899, i, 410; 1900, i, 535).—Phenols dissolved in potassium hydroxide solution behave towards epichlorohydrin in the same way as the alcohols:



The reaction proceeds spontaneously even in the cold, but the yields obtained are small; this result is perhaps related to Menschutkin's laws of etherification of the alcohols, the phenols behaving like tertiary alcohols. The hydroxy-compounds employed were phenol, *m*- and *o*-cresols, thymol, and carvacrol, the following ethers being obtained.

The *diphenyl ether*,  $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{OPh})_2$ , b. p. 287—288°, a liquid of pleasant odour. *Di-o-tolyl ether*,  $\text{C}_{17}\text{H}_{20}\text{O}_3$ , b. p. 296°, a faintly yellow liquid with a pleasant odour. *Di-m-tolyl ether*,  $\text{C}_{17}\text{H}_{20}\text{O}_3$ , b. p. 253—254°, a pale, lemon-yellow liquid. *Dithymyl ether*,  $\text{C}_{23}\text{H}_{32}\text{O}_3$ , a rather dense liquid, b. p. 215°. *Dicarvacryl ether*,  $\text{C}_{23}\text{H}_{32}\text{O}_3$ , b. p. 245—246°, a dense liquid, becoming mobile on heating.

T. H. P.

**Preparation of *o*-Nitro-*p*-cresol.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 206638).—Formerly, the technically important *o*-nitro-*p*-cresol was obtained by boiling the solution of diazotised *o*-nitro-*p*-toluidine; it has now been more easily prepared by nitrating *p*-tolyl carbonate,  $\text{CO}(\text{O}\cdot\text{C}_7\text{H}_7)_2$ , needles, m. p. 117°, when the nitro-group enters the ring in the ortho-position to the methyl group.

*o*-Nitro-*p*-tolyl carbonate,  $\text{CO}(\text{O}\cdot\text{C}_7\text{H}_6\cdot\text{NO}_2)_2$ , yellow needles, m. p. 143—144°, when hydrolysed with boiling aqueous sodium hydroxide or carbonate furnishes *o*-nitro-*p*-cresol, m. p. 77°. F. M. G. M.

**Tetrahydronaphthyl Glycols (cis and trans) and their Combination.** HENRI LEROUX (*Compt. rend.*, 1909, 148, 931—934).—By treating dibromodihydronaphthalene with silver acetate, an ester is obtained which, on hydrolysis, yields a mixture of glycols isomeric with Bamberger's tetrahydronaphthyl glycol,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2\cdot\text{CH}\cdot\text{OH} \\ \text{CH}_2\cdot\text{CH}\cdot\text{OH} \end{array}$  (Abstr., 1893, i, 591). The product has m. p. 110°, and by repeated crystallisation from benzene gives two compounds. The more soluble of these is *trans-tetrahydronaphthyl glycol*, m. p. 118°; the second is a compound, m. p. 140°, formed by union of an equal number of molecules of the *cis*- and *trans*-isomerides. Bamberger's compound appears to be the *cis*-glycol.

*trans*-Tetrahydronaphthyl glycol crystallises in striated tablets; its *diacetate* crystallises in prisms, m. p. 59°. The *dibenzoate* has m. p. 127°. The *diphenylurethane* occurs in needles, m. p. 175°.

The compound of the *cis*- and *trans*-glycols, which has also been obtained by mixing its constituents in benzene solution, differs from the *trans*-compound in being very soluble in water; treatment with acetic anhydride and pyridine leads to the formation of a mixture of *cis*- and *trans*-diacetates. Similar compounds have been obtained by the combination of other *cis*- and *trans*-isomerides; thus the compound of *cis*-hexane-1 : 2-diol with its *trans*-isomeride has m. p. 73°.

W. O. W.

**Formation of an Ether by the Dehydration of the Alcohol by Heat.** PAUL CARRÉ (*Bull. Soc. chim.*, 1909, [iv], 5, 286—287).—*m*-Nitrobenzyl alcohol is converted by distillation into *m*-nitrobenzyl ether,  $O(CH_2 \cdot C_6H_4 \cdot NO_2)_2$ , m. p. 114°, which is changed quantitatively by phosphorus pentachloride into *m*-nitrobenzyl chloride, m. p. 47°.

The ortho- and para-isomerides do not behave in a similar manner on distillation.

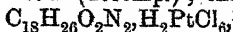
C. S.

**New Method for obtaining Substituted Thiocarbamates of Monohydric Alcohols.** M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 107—108. Compare Orndorff and Richmond, *Abstr.*, 1900, i, 156).—Substituted thiocarbamates of monohydric alcohols may be readily prepared by the action of phenyl or other thiocarbimide on the alkyloxides derived from the alcohols at the ordinary temperature, the reaction being instantaneous and quantitative. With phenylthiocarbimide, menthol gives a compound, m. p. 74—75°; benzyl alcohol, a compound, m. p. 82—82.5°, and  $\alpha$ -terpineol, one, m. p. 109°.

This reaction, which is being extended to other thiocarbimides, and to mercaptans, phenols, and polyhydric alcohols, may be employed for the resolution of racemic alcohols and mercaptans.

T. H. P.

**Aminoaryl Alcohols. I. Preparation of  $\alpha$ -Amino- $\alpha$ -phenylisopropyl Alcohol.** HERMANN EMDE [with E. RUNNE] (*Arch. Pharm.*, 1909, 247, 130—140. Compare *Abstr.*, 1908, i, 203).—Phenylacetone when treated with sodium ethoxide and amyl nitrite yields oximinophenylacetone, together with a substance, m. p. 188°, which crystallises in slender, white needles. Oximinophenylacetone is reduced by stannous chloride, yielding  $\alpha$ -amino- $\alpha$ -phenylacetone, the platinichloride of which crystallises in yellow needles ( $1H_2O$ ), decomposing at 183°, and compact, reddish-brown prisms, decomposing at 194° (compare Kolb, *Abstr.*, 1896, i, 576; Gabriel, *Abstr.*, 1908, i, 466); the *aurichloride* crystallises in flat, golden-yellow needles, m. p. 83°, decomposing at 138—140°.  $\beta$ -Amino- $\beta$ -phenylisopropyl alcohol,  $NH_2 \cdot CHPh \cdot CHMe \cdot OH$ , is prepared by reducing the corresponding ketone with sodium amalgam; it forms flexible, glassy crystals, sinters at 83°, m. p. 85°; the *hydrochloride*,  $C_9H_{13}ON \cdot HCl$ , crystallises in white leaflets, m. p. 170—171° (decomp.); the *platinichloride*,



forms small, orange-red plates, m. p.  $189^{\circ}$  (decomp.); the *aurichloride*,  $C_{16}H_{26}O_2N_2 \cdot HCl \cdot HAuCl_4$ , forms golden-yellow needles, m. p. about  $85^{\circ}$  (decomp.); the *picrate* crystallises in short needles, m. p.  $180-181^{\circ}$  (decomp.). W. H. G.

***l*-Campholic Acid and its Derivatives.** MARCEL GUERBET (*Bull. Soc. chim.*, 1909, [iv], 5, 272-276. Compare this vol., i, 100).—*l*-Campholic acid is obtained in 75% yield by heating *l*-borneol and recently fused potassium hydroxide in a sealed tube for twenty-four hours at  $280^{\circ}$ , dissolving the product in dilute hydrochloric acid and ether, shaking the ethereal solution with dilute sodium hydroxide, and precipitating the *l*-campholic acid from the latter at  $0^{\circ}$  by carbon dioxide. The acid has m. p.  $106-107^{\circ}$ , b. p.  $250^{\circ}$ ,  $[\alpha]_D^{25} -46.5^{\circ}$ , and resembles the *d*-isomeride in its chemical behaviour. The *anhydride*,  $(C_{10}H_{17}O)_2O$ , m. p.  $57-58^{\circ}$ , is obtained by heating the acid with acetic anhydride, and separates unchanged by the spontaneous evaporation of its solution in cold water. The *chloride*,  $C_{10}H_{17}OCl$ , has b. p.  $222^{\circ}$ , and the *amide*,  $C_{10}H_{17}O \cdot NH_2$ , prepared from the chloride and aqueous ammonia in the presence of ether, has m. p.  $78-79^{\circ}$ , and is hydrolysed by alkalis only with difficulty. *l*-Campholic acid cannot be directly esterified. The esters are prepared from the chloride or the anhydride and the corresponding alcohol; the *methyl* ester and the *ethyl* ester have b. p.  $211^{\circ}$  (corr.) and  $228^{\circ}$  (corr.) respectively. C. S.

**Synthesis of Dimethylnorcampholide.** GUSTAV KOMPPA and S. V. HINTIKKA (*Ber.*, 1909, 42, 898-899).—This is a continuation of the investigation of the action of magnesium alkyl derivatives on anhydrides related to camphoric anhydride (compare Abstr., 1908, i, 352), and it has been found that the *dimethylnorcampholide* (annexed formula) prepared from the interaction of magnesium methyl iodide and 1:3-cyclopentanedicarboxylic anhydride is identical with Semmler's lactone of  $\delta$ -hydroxycamphenilonic acid (this vol., i, 170), m. p.  $94.5-95^{\circ}$ , crystallising from light petroleum in large, rectangular plates. W. R.

**Transformation of Pinonic Acid into *m*-Xylylacetic Acid.** PHILIPPE BARBIER and VICTOR GRIGNARD (*Compt. rend.*, 1908, 148, 646-648).—Pinonic acid undergoes an unexpected transformation when heated at  $100^{\circ}$  with water and bromine. After neutralising the product with sodium hydrogen carbonate and filtering, the liquid gives a precipitate of *m*-xylylacetic acid (Claus, Abstr., 1890, i, 979) on the addition of hydrogen chloride. Crude pinonic acid may be used in this preparation. This reaction is in accordance with the accepted constitution for pinonic acid, and is analogous to the conversion of methylheptenone into dihydro-*m*-xylene under the influence of hydrogen bromide.

*Methyl m-xylylaceta*te is a liquid having a raspberry-like odour, b. p.  $120-121^{\circ}/11$  mm. W. O. W.

**Action of Nitric Acid on Benzoyl Chloride in Presence of Acetic Anhydride.** WILLIAM J. KARSLAKE and R. C. HUSTON (*J. Amer. Chem. Soc.*, 1909, 31, 479-483).—Pictet and Genequand

(Abstr., 1902, i, 584) and Pictet and Khotinsky (Abstr., 1907, i, 175) have shown that when acetic acid and acetic anhydride are used as solvents in the nitration of aromatic compounds, the actual nitrating agent is probably either diacetylorthonitric acid or acetyl nitrate, or both. This question has now been studied by means of experiments on the nitration of benzoyl chloride.

When a mixture of benzoyl chloride, acetic anhydride, and nitric anhydride is heated at 60°, oxides of nitrogen are evolved, and a solid residue is obtained, which dissolves in boiling water to form a solution from which benzoic acid separates on cooling. Neither nitroderivatives nor acetyl derivatives of benzoic acid are produced in this reaction.

If benzoyl chloride is warmed at 40° with a mixture of nitric acid and acetic anhydride, *o*-acetylbenzoic acid (acetophenone-*o*-carboxylic acid), benzoic acid, and *m*-nitrobenzoic acid are obtained, the relative amounts of these compounds depending on the proportions of the reagents used. Benzoyl chloride is not capable of acetylation by acetic anhydride alone, or of nitration or acetylation by acetyl nitrate, but by the action of diacetylorthonitric acid it seems to be hydrolysed to benzoic acid, which is then nitrated or acetylated.

Acetophenone-*o*-carboxylic acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , was first obtained by Gabriel and Michael (Abstr., 1878, 229). The *chloride* is an oil; the *amide*, m. p. 116.5°, forms small, colourless prisms, and the anilide melts at 156—157°. The barium, *strontium*, lead, and *silver* salts are described. E. G.

**Preponderance of Temperature in Direct Decompositions :**  
**Case of Benzoic and Salicylic Esters.** ALBERT COLSON (*Compt. rend.*, 1909, 148, 643—645. Compare Abstr., 1908, i, 1).—A continuation of the study of the decomposition of esters by heat. Methyl benzoate differs from its homologues in remaining unaltered at 300—310°; when heated for seven hours at 350°, however, it yields a small quantity of carbon dioxide. Ethyl salicylate decomposes at 300° in accordance with the equation  $\text{C}_9\text{H}_{10}\text{O}_8 = \text{PhOH} + \text{C}_2\text{H}_4 + \text{CO}_2$ . Under the same conditions, methyl salicylate gives carbon dioxide and anisole with small quantities of phenol. Allyl benzoate gives carbon dioxide and a hydrocarbon.

The author considers that these experiments lend support to his contention that temperature is the determining cause of chemical reactions. If this is the case in the classical conversion of aromatic acids into hydrocarbons, the lime acts merely as an accelerating agent. To test this point, ethyl and methyl salicylates were heated with lime in sealed tubes at 235° for seven hours. The tubes were found to contain a considerable amount of carbon dioxide, together with unaltered lime, indicating that neither the lime nor the heat of formation of calcium carbonate should be regarded as the determining cause of the reaction. W. O. W.

**Preparation of Anhydrides of Cyclic and Aliphatic Acids.** AUGUSTE BÉHAL (*Compt. rend.*, 1909, 148, 648—650. Compare this vol., i, 145—164).—When tri-*o*-chlorophenylmethane is boiled with

excess of acetic acid for ten hours, hydrogen chloride is liberated and benzoic acid, benzoic anhydride, acetic anhydride, and acetic benzoic anhydride are formed. Benzoyl chloride also appears to be produced, but cannot be isolated, inasmuch as it reacts rapidly with acetic acid, giving a mixture of the foregoing substances. As in the cases previously studied, certain salts exercise an accelerating influence; thus, in the present instance, 86% of the total amount of hydrogen chloride is evolved in two hours, and the reaction is complete in six hours when carried out in presence of a small quantity of cobalt chloride.

W. O. W.

**Preparation of 3:5-Diiodotyrosine.** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, 59, 320—324).—In the preparation of 3:5-diiodotyrosine (iodogorgonic acid: compare Abstr., 1905, i, 350; Abstr., 1908, i, 420), the formation of resinous products may be avoided by working at 0° and adding iodine until there is a permanent excess.

G. B.

**allo- and iso-Cinnamic Acids.** CARL LIEBERMANN (*Ber.*, 1909, 42, 1027—1036).—Billmann (this vol., i, 155) has shown that the difference between *allocinnamic* and the two *isocinnamic* acids is due to trimorphism. Giesel has now found a quantity of *isocinnamic* acid (m. p. 58°) which has been kept ten to fifteen years in the dark undisturbed; this is shown by crystallographic means to be identical with Liebermann's *iso*-acid. Billmann has shown that all three acids when heated in a steam-drying oven (at 105°) are converted into an acid, m. p. 42°, and this in the fused condition, when inoculated with *isocinnamic* acid (m. p. 58°) or with *allocinnamic* acid, immediately crystallises as a mass of the inoculating acid. These observations are confirmed; both *iso*-acids are not only immediately converted into the *allo*-acid on inoculation, but pass over into it, particularly the *iso*-acid (m. p. 42°), of their own accord.

E. F. A.

**New Synthesis of Inactive αδ-Diaminovaleric Acid and of Proline.** EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1909, 42, 1022—1026).—Benzoylpiperidine is oxidised by permanganate to benzoyl-*d*-aminovaleric acid,  $\text{COPh}\cdot\text{NH}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$ , which, when treated with bromine and phosphorus, forms *α*-bromobenzoyl-*δ*-aminovaleric acid, and this is converted by ammonia into *monobenzoyl ornithine*, from which inactive ornithuric acid (dibenzoyl-αδ-diaminovaleric acid) is easily obtained on benzoylation. The method is analogous to that used by J. von Braun (this vol., i, 229) for the synthesis of lysine from *ε*-benzoylaminoheptonic acid. Bromo-*δ*-benzoyl-aminovaleric acid when boiled with hydrochloric acid yields proline in quantity. It is obtained on bromination of benzoyl-*δ*-aminovaleric acid as an amorphous solid, and forms an amorphous silver salt. The crude product interacts with aqueous ammonia, forming inactive *δ*-benzoylornithine,  $\text{COPh}\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ ; this crystallises in colourless plates, m. p. 260° (decomp.), and is very similar to the active form (Fischer, Abstr., 1901, i, 192); the yield represents about 20% of the original weight of piperidine taken.

E. F. A.

[Esters of Salicylic Acid and the Higher Aliphatic Acids.] NATHAN SULZBERGER (D.R.-P. 206056).—The esters of salicylic acid and the higher aliphatic acids are easily absorbed by the skin without producing local irritation, and within the organism they undergo fission, giving rise to salicylic acid. They are produced by condensing the alkyl salicylates with the alkali salts of oleic, stearic, erucic, brassidic, elaidic, ricinolic, palmitic, and hydroxystearic acids, either alone or in the presence of phosphoryl chloride.

*Ethyl oleylsalicylate* [*o-oleoyloxybenzoate*],  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{33}$ , an oily mass solidifying and melting at  $10^\circ$ , and *ethyl stearylsalicylate* [*o-stearyloxybenzoate*],  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{35}$ , a white, crystalline mass, m. p. 48—49°, produced in this way, are substances having an antiseptic action. F. M. G. M.

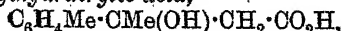
Action of a Mixture of Ethyl  $\alpha$ -Bromopropionate and *p*-Tolualdehyde on Zinc. M. STRSCHALKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 18—22).— $\beta$ -*p*-Tolyl- $\alpha$ -methylhydracrylic acid,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , prepared by the action of zinc on a mixture of ethyl  $\alpha$ -bromopropionate and *p*-tolualdehyde in presence of sulphuric acid and decomposing the compound obtained by means of water, crystallises from water in hexagonal prisms, m. p. 108—110°, and has the normal molecular weight in boiling ether. Its sodium ( $\text{H}_2\text{O}$ ) and silver salts were prepared and analysed. The ethyl ester,  $\text{C}_{13}\text{H}_{18}\text{O}_3$ , b. p. 182°/125 mm.,  $n_D^{20}$  1.5022,  $D_4^{20}$  slightly greater than 1, is a viscous liquid with an odour resembling that of honey, and is readily soluble in alcohol or ether.

On heating the hydroxy-acid with sulphuric acid, it yields a neutral unsaturated product, b. p. about 200°, which should be, and is probably, *a-p*-tolylpropylene (compare Errera, Abstr., 1885, 655). T. H. P.

Action of Zinc on a Mixture of *p*-Tolyl Methyl Ketone and Ethyl Bromoacetate. I. MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 56—66).—The action of zinc on a mixture of *p*-tolyl methyl ketone and ethyl bromoacetate yields the ester of  $\beta$ -*p*-tolyl- $\beta$ -methylhydracrylic acid, which, however, readily loses water, giving an unsaturated acid,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H} = \text{C}_6\text{H}_4\text{Me}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$ .  
 $\beta$ -*p*-Tolyl- $\beta$ -methylhydracrylic acid can, however, be obtained by isolating and hydrolysing its silver salt.

$\beta$ -*p*-Tolyl- $\beta$ -methylhydracrylic acid,

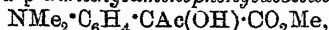


is a faintly yellow, viscid liquid, which, on distillation or on boiling with dilute sulphuric acid, yields *a-p*-tolylpropylene. The silver salt was prepared.

$\beta$ -*p*-Tolylcrotonic acid,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , crystallises from water in needles and from alcohol in prisms, rhombs, or needles, m. p. 132—134°. Its silver, calcium,  $\text{Ca}(\text{C}_{11}\text{H}_{11}\text{O}_2)_2\cdot 3\text{H}_2\text{O}$ , barium, and potassium salts were prepared. On dry distillation, the acid yields  $\beta$ -*p*-tolylpropylene (compare Errera, Abstr., 1891, 1020). The ethyl ester,  $\text{C}_{13}\text{H}_{18}\text{O}_2$ , is a colourless, mobile liquid, b. p. 172°/25 mm.,  $D_4^{23}$  1.02091, with a faint odour recalling that of methyl *p*-tolyl ketone, and dissolves readily in alcohol, ether, or benzene. T. H. P.

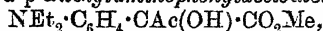
Condensation of Methyl Diketobutyrate with Aromatic Hydrocarbons and Amines. ALFRED GUYOT and V. BADONNEL (*Compt. rend.*, 1909, 148, 847—849. Compare this vol., i, 158, 236).

—Methyl  $\alpha$ -hydroxy- $\alpha$ - $p$ -dimethylaminophenylacetoacetate,



obtained by the interaction of molecular proportions of dimethylaniline and methyl diketobutyrate in acetic acid solution, crystallises from carbon disulphide in colourless leaflets, m. p.  $81^\circ$ .

Methyl  $\alpha$ -hydroxy- $\alpha$ - $p$ -diethylaminophenylacetoacetate,



prepared from diethylaniline and methyl diketobutyrate, crystallises in small prisms, m. p.  $56^\circ$ .

These two esters are hydrolysed quantitatively into acetic acid and dialkylaminophenylglycollic acid,  $\text{NR}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$ , by aqueous potassium hydroxide, whilst with hot concentrated sulphuric acid a dialkylamino-derivative of benzaldehyde,  $\text{NR}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ , is obtained. Cupric acetate oxidises the esters to methyl dialkylaminophenylglyoxylates,  $\text{NR}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO}_2\text{Me}$ . With phenylhydrazine, the esters give the corresponding simple hydrazones, m. p.  $106^\circ$  and  $153^\circ$  respectively.

Diketobutyric esters also condense with aromatic hydrocarbons, giving, firstly, a hydroxyphenylacetoacetic ester, such as  $\text{OH} \cdot \text{CPhAc} \cdot \text{CO}_2\text{R}$ , which then fixes a second molecule of hydrocarbon, forming an ester of diphenylacetoacetic acid,  $\text{CPh}_2\text{Ac} \cdot \text{CO}_2\text{R}$ ; thus toluene yields (1) methyl  $\alpha$ -hydroxy- $p$ -tolylacetoacetate,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{Me}$ , a colourless oil, b. p.  $190^\circ/15$  mm., and (2) methyl ditolylacetoacetate,  $\text{C}(\text{Ac}(\text{C}_6\text{H}_4\text{Me}))_2 \cdot \text{CO}_2\text{Me}$ , which crystallises in colourless prisms, m. p.  $119^\circ$ , b. p.  $235^\circ/15$  mm., and is resolved quantitatively into acetic acid and ditolylacetic acid by means of alcoholic potassium hydroxide.

T. H. P.

3-Amino- $o$ -phthalic Acid and Certain of its Derivatives. MARSTON T. BOGERT and FAREL LOUIS JOUARD (*J. Amer. Chem. Soc.*, 1909, 31, 483—490).—In an earlier paper (*Abstr.*, 1908, i, 651), a description has been given of 4-amino- $o$ -phthalic acid and its derivatives. The work has now been extended to the 3-amino-compounds.

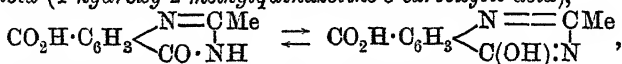
Onnertz (*Abstr.*, 1902, i, 101) first prepared 3-amino- $o$ -phthalic acid, but was unable to purify it. It has now been obtained in the pure state by reducing the corresponding nitro-acid with tin and hydrochloric acid. The compound is a white, crystalline solid, which gradually becomes yellow. When heated rapidly, it melts at  $177^\circ$  (decomp.), or when heated slowly, at  $191^\circ$  (decomp.). If the acid is boiled with water, a fluorescent solution is obtained, which deposits orange-yellow crystals of a substance, m. p.  $240^\circ$  (decomp.), which has not been identified. The hydrochloride of the acid, m. p.  $227^\circ$  (corr.), and the potassium hydrogen, ammonium hydrogen, silver, and barium salts are described. The hydrochlorides of the methyl and dimethyl esters have m. p.  $153^\circ$  (corr.) and  $172$ — $174^\circ$  (decomp.) respectively.

Methyl 3-acetyl-amino- $o$ -phthalate,  $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2$ , m. p.  $92$ — $93^\circ$  (corr.), exhibits strong triboluminescence, even under water.

3-Amino-*o*-phthalic anhydride, m. p. 193—194° (corr.), crystallises in pale yellow needles; its acetyl derivative melts at 185—186° (corr.).

3-Amino-*o*-phthalimide has m. p. 266—267° (corr.); its *hydrochloride* and *potassium* derivative are described. 3-Acetylamino-*o*-phthalimide melts at 242° (corr.), and the *diacetyl* compound at 152—154° (corr.). 3-Phenylcarbamino-*o*-phthalimide,  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot (\text{CO})_2 \cdot \text{NH}$ , sinters at about 260°, and darkens and melts at about 335°. 3-Amino-*o*-phthalanil melts at 186—188° (corr.), and its acetyl derivative at 195·5° (corr.). 3-Acetylaminophthal-*o*-tolyl, m. p. 214—215° (corr.), forms straw-coloured prisms. The *phenylhydrazide* of 3-amino-*o*-phthalic acid, m. p. 284—285° (decomp.), reacts with acetic anhydride with formation of a *substance*, m. p. 223—224° (corr.), which has not been further investigated.

Methyl 3-azophthalate,  $\text{N}_2[\text{C}_6\text{H}_3(\text{CO}_2\text{Me})_2]_2$ , m. p. 224—225° (corr.), obtained by the action of aluminium amalgam on methyl *o*-nitrophthalate, forms pale salmon needles. 2-Methyl-4-quinazoline-5-carboxylic acid (4-hydroxy-2-methylquinazoline-5-carboxylic acid),



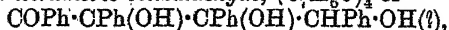
m. p. 342° (decomp.), obtained by boiling acetylamino-*o*-phthalimide with potassium hydroxide solution and acidifying the product, crystallises in colourless needles; its *methyl* ester melts at 273—274° (corr.).

E. G.

Condensation of Mesoxalic Esters with Phenolic Esters. ALFRED GUYOT and G. ESTÉVA (*Compt. rend.*, 1909, 148, 719—720. Compare this vol., i, 158, 236).—In presence of concentrated sulphuric acid, mesoxalic esters undergo condensation with phenolic ethers, giving a mixture of two products, namely, a substituted phenyltartronic ester and a substituted diphenylmalonic ether. When sulphuric acid and the phenolic ester are present in excess, only the latter is obtained. The following compounds were obtained by condensing methyl or ethyl mesoxalate with anisole and phenetole. Methyl *p*-methoxyphenyltartronate,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C(OH)(CO}_2\text{Me)}_2$ , long needles, m. p. 118°. Methyl *di-p*-methoxymalonate,  $\text{C(C}_6\text{H}_4 \cdot \text{OMe)}_2(\text{CO}_2\text{Me)}_2$ , pearly leaflets, m. p. 90°; the *ethyl* ester occurs in brilliant spangles, m. p. 72°. Methyl *p*-ethoxyphenyltartronate,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{C(OH)(CO}_2\text{Me)}_2$ , prisms, m. p. 112°. Methyl *di-p*-ethoxyphenylmalonate,  $\text{C(C}_6\text{H}_4 \cdot \text{OEt)}_2(\text{CO}_2\text{Me)}_2$ , leaflets, m. p. 118°; the *ethyl* ester occurs in brilliant spangles, m. p. 92·5°.

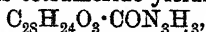
W. O. W.

Chemical Actions of Light. XIII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 216—220. Compare *Abstr.*, 1908, i, 555).—One hundred grams of benzaldehyde were exposed to the action of light for two years and five months, at the end of which time it was almost completely resinsified. It was then found to contain (1) the trimeric benzaldehyde obtained by Mascarelli (*Abstr.*, 1906, i, 962) by the interaction of benzaldehyde and iodoxybenzene under the influence of light; (2) benzoic acid; (3) hydrobenzoin; (4) a *tetrameric benzaldehyde*,  $(\text{C}_7\text{H}_6\text{O})_4$  or



\* and *Ber.*, 1909, 42, 1886—1891.

which is a white powder, m. p. 160—170°, and has the normal molecular weight in acetic acid, but gives a value corresponding with the formula  $(C_7H_6O)_9$  in benzene; this tetrameride yields a *semicarbazone*,



which forms a white powder, m. p. 232° (compare Abstr., 1903, i, 562).

Dibenzylideneacetone, when exposed to the action of sunlight in alcohol, in which it is mainly suspended; is converted into a resin, which separates from a mixture of ether and light petroleum as an almost white powder, m. p. 125—135°, having the composition  $(C_{17}H_{15}O)_2$ .

The greater reactivity of *isosafole* containing a propenyl group compared with *safrole* containing an allyl group is also evident when these two compounds are exposed to the action of light in presence of a little iodine; the *safrole* then remains practically unaltered, whilst the *iso*-compound is transformed into a resin from which *disosafole* can be separated in small proportion (compare Angeli and Mola, Abstr., 1895, i, 24).

A similar difference is exhibited in the behaviour of the methyl ethers of eugenol and *isoeugenol* in presence of iodine and under the influence of light. The former undergoes no change even after prolonged exposure, but the latter yields a *compound*, crystallising from methyl alcohol in slender needles, m. p. 96°, and having the composition of *disoeugenol* methyl ether, although apparently not identical with the one described by Széki (Abstr., 1906, i, 660) and by Francesconi and Puxeddu (this vol., i, 226).

Under the influence of sunlight, benzaldehyde condenses with many different compounds (compare Klinger and Standke, Abstr., 1891, 900; Klinger and Kolvenbach, Abstr., 1898, i, 467; Benrath, Abstr., 1906, i, 535). The authors find that benzaldehyde forms condensation products with both *safrole* and *isosafole* having the composition  $C_7H_6O, C_{10}H_{10}O_2$ , the former having m. p. 150—180°, and the latter, m. p. 170—180°.

T. H. P.

**Separation of *o*- and *p*-Chlorobenzaldehydes.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 207157).—*o*- and *p*-Chlorobenzaldehydes can be separated by taking advantage of the slight difference in their boiling points: the ortho, b. p. 108°, and the para, b. p. 213°/748 mm. The first fraction when cooled to -20° gives solid *o*-chlorobenzaldehyde (m. p. +11°, and not -4°), whilst the end fraction when similarly refrigerated yields the para-isomeride.

F. M. G. M.

**Variations in the Density of Anisaldazine at the Clearing Temperature.** F. CONBAT (*Physikal. Zeitsch.*, 1909, 10, 202—206).—The variation of the density of anisaldazine with the temperature in the neighbourhood of the clearing point has been investigated by means of a dilatometer. Whereas the isotropic modification is quite normal in its behaviour, it is found that the anisotropic form shows an abnormally large rate of increase in volume as the clearing temperature is approached. In addition to the sharp change in the density which accompanies the transition from the anisotropic to the

isotropic modification, there is a comparatively small change which takes place before the transition temperature is reached

H. M. D.

**Aldehydic Compounds.** ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 221—225).—Salicylaldehyde does not give a hydroxamic acid when treated with dihydroxyammonia in presence of alkali, although the corresponding ethoxy-aldehyde readily reacts. Negative results are also given by protocatechualdehyde and its carbonate.

*m*-Hydroxybenzaldehyde, however, yields *m*-hydroxybenzhydroxamic acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{OH}$ , which separates from ethyl acetate in large crystals, m. p. about  $72^\circ$ , dissolves readily in water, turns red in the air, and gives an intense violet coloration with ferric chloride; dilute sulphuric acid hydrolyses it, yielding hydroxylamine and *m*-hydroxybenzoic acid. It yields a green copper salt. *m*-Hydroxybenzhydroxamic acid is also obtained in quantitative yield from ethyl *m*-hydroxybenzoate by the action of an alcoholic solution of hydroxylamine in presence of sodium ethoxide (compare Jeanrenaud, *Abstr.*, 1889, 870).

The aldehydes of the pyrrole and indole groups, which can be obtained by treating the pyrroles and indoles with chloroform and potassium hydroxide, do not yield hydroxamic acids (compare Angelo and Marchetti, *Abstr.*, 1907, i, 551; this vol., i, 12). But the authors have obtained, by the action of amyl formate on 2-methylindole in presence of sodium ethoxide, a sodium salt of methylindolealdehyde, which they regard as a hydroxymethylene derivative of the constitution  $\text{N} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CH} \end{smallmatrix} \text{C}:\text{CH}\cdot\text{OH}$ . Analogy is drawn between the aromatic hydroxyaldehydes and certain of the nitroso-indoles, phenols, and naphthols, which must be regarded as oximes, the new arrangement of the molecules being determined by the iminic hydrogen in the case of the indoles, and by the phenolic hydrogen in the case of the phenols and naphthols. The view that a similar rearrangement is produced with the aromatic hydroxyaldehydes, owing to the presence of the hydroxyl hydrogen, is supported by the fact that, when the hydroxyl is converted into alkoxy, these compounds give hydroxamic acids.

Vanillin does not yield a hydroxamic acid, but *isovanillin* readily does so.

T. H. P.

**Behaviour of the Compounds  $\text{CRPh}\cdot\text{NOH}$  towards Nitrogen Peroxide.** GIACOMO PONZIO (*Gazzetta*, 1909, 39, i, 324—326).—When, in compounds of the formula  $\text{CRPh}\cdot\text{NOH}$ ,  $\text{R}=\text{Ph}$  or  $\text{Me}$ , nitrogen peroxide converts them into dinitro-derivatives, whilst when  $\text{R}=\text{COPh}$ , oxidation to benzil takes place. The present experiments show that when  $\text{R}=\text{CH}_2\cdot\text{OH}$ , a dinitro-compound is formed, whilst when  $\text{R}=\text{CO}_2\text{H}$  a dioxime-peroxide is obtained. In the latter case, analogy with the formation of aliphatic nitrolic acids indicates that benznitrolic acid,  $\text{CHPh}\cdot\text{N}_2\text{O}_3$ , is an intermediate product.

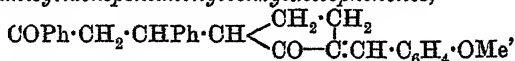
Oximinophenylacetic acid,  $\text{CO}_2\text{H}\cdot\text{CPh}\cdot\text{NOH}$ , reacts with nitrogen peroxide in cold ethereal solution, yielding diphenylglyoxime peroxide,

$\begin{array}{c} \text{CPh:NO} \\ | \\ \text{CPh:NO} \end{array}$  Benzoylcarbinoloxime,  $\text{OH}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{NOH}$ , yields phenyl-dinitromethane when similarly treated. C. H. D.

Methods for the Preparation of Stereoisomeric Benzylidene-anisylidenecyclopentanones and Similar Unsymmetrical Derivatives of Cyclic Ketones. HANS STOBBE (*Ber.*, 1909, 42, 921—928).—Stereoisomeric unsymmetrical substituted cyclic ketones

of the type  $\text{CHR}'\cdot\text{C} \begin{array}{l} \text{CH}_2\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{C}\cdot\text{CHR}'' \end{array}$  where  $\text{R}'$  and  $\text{R}''$  represent two aryl groups, can be synthesised by either of the following methods: (1) A compound of the type of Stobbe and Volland's (*Abstr.*, 1902, i, 472; 1903, i, 115)  $\beta$ -cyclopentanonylbenzylacetophenone is condensed with anisaldehyde, and the resulting anisylidene derivative or derivatives decomposed by distillation under reduced pressure. (2) An aqueous-alcoholic solution of anisaldehyde and benzaldehyde is condensed with cyclopentanone in the presence of 10% sodium hydroxide solution at the ordinary temperature.

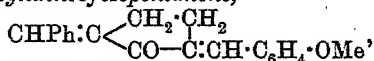
[With ROBERT GEORGI and RICHARD HÄRTEL].—Anisaldehyde condenses with  $\beta$ -cyclopentanonylbenzylacetophenone in the presence of a few drops of sodium hydroxide solution, yielding two stereoisomeric  $\beta$ -anisylidenepentanonylbenzylacetophenones,



termed anisylidene diketones *A* and *B*, which can be separated by crystallisation from dilute alcohol, in which the *A* compound, m. p. 126°, is more readily soluble than the *B* compound, m. p. 146°. Both compounds are colourless, and form yellow additive compounds with sulphuric acid. When the condensation takes place at 15—20°, only some 10—15% of *B* is obtained, whereas at 50° this compound is the chief product. The two are stereoisomeric, as they can each be transformed into the other by the following methods: Action of light on the crystals or on their benzene solutions; action of heat or boiling their benzene solutions with a small amount of iodine.

When heated, both diketones are decomposed, and when distilled under 12 mm. pressure yield unaltered substance, benzylidene-anisylidenecyclopentanone and a stereoisomeride, dianisylidenecyclopentanone, and benzylideneacetophenone.

*Benzylideneanisylidenecyclopentanone*,



is readily soluble in alcohol, from which it separates in yellow lamellæ, m. p. 153°; the *stereoisomeride* crystallises from alcohol, in which it is sparingly soluble, in dark lemon-yellow, felted needles, m. p. 147°. Both compounds combine with bromine or sulphuric acid, and may be transformed each into the other. J. J. S.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. III. EMIL FISCHER (*Ber.*, 1909, 42, 1015—1022. Compare *Abstr.*, 1908, i, 892; this

vol., i, 161).—*p*-Methylcarbonatobenzoyl chloride combines with benzene in presence of aluminium chloride, forming *p*-methylcarbonatobenzophenone,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , which yields, on hydrolysis, the known *p*-hydroxybenzophenone. In a similar manner, 3:4:5-trihydroxybenzophenone has been obtained from 3:4:5-trimethylcarbonatobenzoyl chloride. This differs from the isomeric alizarin-yellow, and confirms the supposition that alizarin-yellow is 2:3:4-trihydroxybenzophenone; it should be possible to prepare it from pyrogallol-carboxylic acid.

*p*-Methylcarbonatobenzophenone crystallises in colourless, obliquely-cut, microscopic prisms or needles, m. p. 94—95° (corr.), to a colourless liquid; it is hydrolysed to *p*-hydroxybenzophenone, m. p. 135° (corr.), by heating with sodium hydroxide.

3:4:5-Trihydroxybenzophenone, prepared by the interaction of benzene, aluminium chloride and 3:4:5-trimethylcarbonatobenzoyl chloride at 70°, and subsequent hydrolysis, crystallises with  $1\text{H}_2\text{O}$  in faintly yellow, thin, glistening plates, but is colourless when anhydrous. It has m. p. 177—178° (corr.), reduces silver nitrate and Fehling's solution, and, like alizarin-yellow, dyes with mordants.

Gallacetophenone semicarbazone is a bright yellow, glistening, crystalline powder consisting of microscopic, short, thick prisms or tablets, m. p. 225° (quickly heated) to a red liquid and decomposes at a higher temperature. The so-called monoacetylpyrogallol obtained by Einhorn and Hollandt (Abstr., 1898, i, 577) is shown to be in reality gallacetophenone.

Ethyl 3:4:5-trimethylcarbonatobenzoate,  $\text{C}_6\text{H}_2(\text{O}\cdot\text{CO}_2\text{Me})_3\cdot\text{CO}_2\text{Et}$ , forms colourless, thin prisms or needles, m. p. 86—87° (corr.); on cautious hydrolysis, ethyl gallate, m. p. 154—155° (corr.), is obtained.

E. F. A.

Preparation of Alkyl- and Aryl-aminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 205881).—The alkyloxyanthraquinones when heated with primary arylamines, or primary or secondary alkylamines, give rise to aryl- and alkyl-aminoanthraquinone derivatives respectively. The dimethyl or diethyl ethers of quinizarin when heated with *p*-toluidine give rise to quinizarin-green.

1:4-Di-*p*-tolylaminoanthraquinone is similarly obtained by heating with *p*-toluidine at 160—180° the methyl ether of 1-nitro-4-hydroxyanthraquinone.

Other instances of this condensation are described, but the products have already been prepared. F. M. G. M.

Action of Potassium Hydroxide on Borneol, Camphor, and isoBorneol; Racemic Campholic Acid. MARCEL GUERBET (Compt. rend., 1909, 148, 720—723; J. Pharm. Chim., 1909, 29, 321—324. Compare Abstr., 1908, i, 100).—The production of campholic acid by the action of potassium hydroxide on borneol has been described in a previous communication; it is now found that the product of the reaction invariably contains camphor.

Campholic acid, which is obtained from camphor in small yield by Delalande's reaction (Ann. Chim. Phys., 1841, [iii], i, 120), can be

prepared in practically theoretical yield by heating camphor with twice its weight of fused potassium hydroxide at 280—290° in a sealed tube. A small amount of *isocampholic acid* is formed simultaneously. Under the same conditions, *isoborneol* yields a mixture of *r*-borneol, *r*-camphor, and *r*-campholic acid; the latter, which is identical with the racemic acid prepared by mixing equal parts of the *d*- and *l*-acids, crystallises in transparent, hexagonal tablets, m. p. 109°. It is less soluble in alcohol than either of the active acids. The *sodium salt* crystallises with 8H<sub>2</sub>O. The *anhydride* has m. p. 66°. The *amide* has m. p. 90°. W. O. W.

**Preparation of *iso*Bornyl Esters of Fatty Acids.** CHARLES WEIZMANN and THE CLAYTON ANILINE Co. (D.R.-P. 207155).—In the presence of a small proportion of a metallic salt, such as anhydrous zinc chloride, pinene hydrochloride and boiling glacial acetic acid readily condense, giving a yield of about 70% of *isobornyl acetate*, suitable for the production of camphor. Other fatty acids, such as formic and butyric acids, may be employed in this condensation.

F. M. G. M.

**Preparation of *iso*Bornyl Esters from Camphene and Monobasic Organic Acids.** ALBERT VERLEY, EDOUARD URBAIN, and ANDRÉ FEIGE (D.R.-P. 207156).—Aqueous sulphuric acid (4·5 parts of 60—66% H<sub>2</sub>SO<sub>4</sub>) is shaken thoroughly at 20—30° with camphene (1 part) and concentrated acetic acid (1 part), and the mixture then allowed to settle into two layers, the upper of which consists of *isobornyl acetate*, with a trace of borneol, whilst the lower, containing the sulphuric and unaltered acetic acids, is employed in subsequent operations. *iso*Bornyl formates, propionates, and butyrates can be prepared similarly.

F. M. G. M.

**Fenchyl Derivatives.** IWAN L. KONDAKOFF (*J. pr. Chem.*, 1909, [ii], 79, 271—280).—The solid chloride obtained from fenchyl alcohol is regarded as an impure bornyl chloride by Wallach, who doubts the existence of a solid fenchyl chloride corresponding with fenchyl alcohol.

The author, however, by treating the chloride or bromide obtained from *l*-fenchyl alcohol with alcoholic potassium hydroxide, obtains an undecomposable residue, from which the solid chloride or bromide is isolated; this chloride is regarded as a true fenchyl chloride on account of its m. p., 92° (lower than that of bornyl chloride; the preceding bromide also has m. p. 65°, whilst bornyl bromide has m. p. 90°), its inability to yield camphene, and its property of giving, in addition to liquid hydrocarbons, a mixture of fenchyl alcohol and fenchone.

A new solid, *fenchyl chloride*, has been prepared from *l*-fenchyl alcohol. It is purified by fractional distillation and freezing, and has m. p. 22°, b. p. 80—82°/11 mm., D<sub>20</sub> 1·004, *n*<sub>D</sub> 1·4802, and [α]<sub>D</sub><sup>20</sup> -8·89°, is not completely changed to fenchene by alcoholic potassium hydroxide, and at 180° yields fenchyl (and *isofenchyl*?) alcohol and a *fenchene*, which has b. p. 155—160°, D<sub>15</sub><sup>25</sup> 0·869, *n*<sub>D</sub> 1·468802, and [α]<sub>D</sub> -29·49°. The paper concludes with a reply to Wallach's contention that *isofenchyl alcohol*, which yields *isofenchone* by oxidation, must be a secondary and not a tertiary alcohol. C. S.

**Constituents of Essential Oils.** *enol*-Camphenilanaldehyde Acetate and Further Derivatives of Camphenilanaldehyde. Production of Terpinolene by the Inversion of Carvenene (Terpinene?). FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 962—966. Compare this vol., i, 239; Bredt, *Abstr.*, 1900, i, 134).—It is shown that the camphene nucleus remains unchanged in the formation of camphenilanaldehyde from camphene, because camphenilanaldehyde when treated with acetic anhydride and sodium acetate yields *enol-camphenilanaldehyde acetate*,  $C_9H_{14} \cdot CH \cdot OAc$ , a colourless oil, b. p. 113—116°/10 mm.,  $D_{20}$  1.0125,  $n_D$  1.4816, which, when oxidised by ozone, yields camphenilone. The acetate is reduced by sodium and alcohol, yielding *camphenilyl alcohol*,  $C_{10}H_{17} \cdot OH$ , a colourless solid, m. p. about 58—59°, b. p. 105—106°/10 mm.; the same compound is produced by reducing the aldehyde in the same manner; it is converted by phosphorus pentachloride into *camphenilyl chloride*,  $C_{10}H_{17}Cl$ , a colourless liquid, b. p. 83—85°/10 mm.,  $D_{20}$  0.9909,  $n_D$  1.4862, which, when reduced with sodium and alcohol, yields camphene together with a small quantity of *isocamphene*.

*Inversion of Carvenene.*—Carvenene prepared from carvenone does not yield any terpinolene tetrabromide when treated with bromine. When inverted with alcoholic sulphuric acid, it yields *isocarvene* (compare this vol., i, 171), which, when treated with bromine, yields a considerable quantity of terpinolene tetrabromide. If pure *isocarvenene* ( $\Delta^{1:4}$ -dihydrocymene) should not yield terpinene nitrosite, we have the transition: terpinolene  $\longleftrightarrow$  carvenene. W. H. G.

**Essential Oils.** HEINRICH HAENSEL (*Haensel's Bericht*, October-March, 1909. Compare this vol., i, 111).—Oil from the leaves of the marsh mallow (*Althaea officinalis*) has been obtained for the first time; yield 0.022%,  $D^{20}$  0.9209, acid number 88.7, saponification number 122.6, ester number 33.9; it appears to contain valeric and palmitic acids as constituents. *Angelica-root oil* (*loc. cit.*), yield 0.22%,  $D^{15}$  0.8580, consists chiefly of terpenes resembling phellandrene. *Cardamom oil*, freed from terpene, has  $D$  0.948 and  $n_D + 45.93^\circ$ ; the terpene constituent separated therefrom has  $D$  0.846,  $n_D - 1.76^\circ$ . *Lemon oil* from Barcelona is colourless and has a faint aroma,  $D^{20}$  0.8524,  $n_D^{21} + 35.65^\circ$ ; when redistilled and dried  $n_D^{17} + 21.16^\circ$ ,  $n_D^{20} + 20.71$  (calc.); it apparently is largely adulterated. *Cubebs oil*, when obtained terpene-free, has  $D^{15}$  0.9428,  $n_D^{20} - 10.05^\circ$ ; the terpenes obtained therefrom have  $D^{15}$  0.8662,  $n_D^{20} - 15.45^\circ$ . *Pine oil* usually contains such a large proportion of terpene that it requires highly rectified spirit for its solution; to avoid this it has now been prepared terpene-free, and has  $D$  0.9384,  $n_D - 15.56^\circ$ , ester content 39.2%, compared with the ordinary oil  $D$  0.8740,  $n_D - 51.24^\circ$ , ester content 9.8%. *Ginster oil* (*Abstr.*, 1903, i, 187), from *Spartium scoparium*, yield 0.031%, is a brown, strongly acid-smelling substance,  $D^{15}$  0.8673, which partly solidifies at 0°. This oil gave an acid number 58.6, saponification number 88, and an ester number 29.4; it contained furfuraldehyde, and when hydrolysed gave palmitic acid and a white, solid paraffin, which separated from alcohol in needles, m. p. 48—49°. *Guaiacum-wood oil*, when shaken with ether and recrystallised from alcohol,

yields guaiol, which gives dihydroguaiene, b. p.  $12^{\circ}/11$  mm., when warmed with zinc dust. Guaiol methyl ether has b. p.  $141-143^{\circ}/9$  mm. *Hazel-nut-leaf oil*, prepared from the dried leaves of *Corylus Avellana*, yield 0.0425%, is a light brown, acid-reacting substance, only liquid when warm. It has a remarkably persistent aromatic odour, f. p. about  $30^{\circ}$ ,  $D^{25}$  0.8844, acid number 60.4, saponification number 85, ester number 24.6, after acetylation 158. This oil seems to contain a considerable quantity of free acids and alcohols, and when hydrolysed gave palmitic acid. *Oil from Vitex agnus castus* (sensitive plant), procured from Turkey, was obtained by steam distilling the leaves; yield 0.36%. It is a reddish-brown liquid possessing a strong odour resembling camphor;  $D^{20}$  0.8993, acid number 5, saponification number 25.8, ester number 20.8, after acetylation 56.5. When saponified and distilled, palmitic acid, terpenes, cineol, and other substances were obtained. *Oil of cloves*, from Seychelles, had  $D^{20}$  1.031,  $D^{15}$  1.0349,  $\alpha_D - 0.49^{\circ}$ , and contained 80% eugenol, but no furfural. The terpene-free oil is optically inactive, has  $D^{15}$  1.0695, and contains 86.12% eugenol. *Italian peppermint oil*, when freed from terpene, has been found to have somewhat different physical properties from that previously given (*loc. cit.*), namely,  $D^{20}$  0.9014,  $\alpha_D - 26.29^{\circ}$ , ester number 15.0, after acetylation 185.5, content of esterified menthol 5.30%, content of free menthol 55.86%. The isolated terpenes have  $D^{20}$  0.862 and  $\alpha_D - 12.75^{\circ}$ . *Sweet-orange oil* is found to vary somewhat considerably in physical properties according to the district in which the fruit is grown. *Bitter-orange oil*, when terpene-free, has  $D$  0.9038,  $\alpha_D^{18} + 11.80^{\circ}$ ; the isolated terpene portion has  $D$  0.8489 and  $\alpha_D^{17} + 96.18^{\circ}$ . When prepared from unripe fruit this terpene-free oil has  $D$  0.9179 and  $\alpha_D + 9.63^{\circ}$ . *Rosemary oil*, when purified and when freed from terpene, has respectively  $D^{15}$  0.9090 and 0.9376,  $\alpha_D + 5.03^{\circ}$  and  $+ 7.35^{\circ}$ , ester number 8.5 and 9.0, after acetylation 37.9 and 53.6, content of esterified borneol 2.97% and 3.15%, content of free borneol 10.92% and 16.27%, and the terpene-free oil boils at a higher temperature than oil which is only purified. Terpene-free *Star anise oil* has  $D^{22}$  0.9856,  $\alpha_D^{20} + 0.14^{\circ}$ , freezing point  $+ 18.5^{\circ}$ .

J. V. E.

**Essential Oils.** SCHIMMEL & Co. (*Bericht*, April, 1909. Compare this vol., i, 112).—*Andropogon oil*, No. 2, obtained from a different plant to that giving the oil previously described (*loc. cit.*), was pale yellow, having an odour resembling aliphatic aldehydes and geraniol,  $D^{15}$  0.9961,  $\alpha_D - 2^{\circ}$ ,  $n_D^{20}$  1.51236, acid number 3.6, ester number 7.3. It probably contains a small quantity of decaldehyde. *Oil of Artemisia lavandulaefolia*, obtained from wild Java plants, has  $D^{26}$  0.924,  $\alpha_D - 7.5^{\circ}$ , and, when cooled, partly solidifies to a crystalline substance,  $C_{12}H_{14}O_2(?)$ . *Basilicum oil* (Abstr., 1907, i, 66), from *Ocimum minimum*, grown in the south of France, was identical in some respects with the oil from *Ocimum basilicum*, but differs therefrom in chemical composition. It contains 14% eugenol and probably linalool;  $D^{15}$  0.9102,  $\alpha_D - 11.97^{\circ}$ , acid number 5.3, ester number 12.5, phenol content 14%. *Lemon-scented bay oil*, obtained from *Pimenta acris citrifolia*, is found to have  $D^{25}$  0.882,  $\alpha_D - 0.6^{\circ}$ , and probably

65% citral. Leaves from the Isle of Tortola yield 1.11% of a pale yellow oil possessing a strong odour of lemon, and having  $D_{16}^{27}$  0.8937,  $n_D$  - 0.16°, citral content 44%, phenol content 10%. *Calmus oil*.—Two samples obtained from Java were yellow, possessing a faint calmus odour; the constants were: (I)  $D^{15}$  1.0783,  $n_D$  + 0.9°,  $n_D^{20}$  1.55043, ester number 12; (II)  $D^{15}$  1.0771,  $n_D$  + 0.85°,  $n_D^{20}$  1.55065, thus showing a considerable difference from ordinary calmus oil. A detailed account is given of the preparation of *Cananga oil* from the expressed plant juice. The composition of this oil seems to vary with the district in which the tree is grown and also with the climate. The difference between *Cananga oil* and *Ylang-ylang oil* lies in the fact that the former contains less ester, less alcohol, and more sesquiterpene than the latter. Under certain conditions of distillation it is considered possible to obtain the more valuable *Ylang-ylang oil* from cananga sap instead of *Cananga oil*.

*Copaiba Balsam Oil*.—It has been shown that several so-called Copaiba oils are mixtures of African Copaiba oil and Gurjun balsam oil. The constants for this oil are now given as  $D^{15}$  0.9692,  $n_D$  - 41.33°, acid number 60.75, saponification value (cold) 64.72. By means of steam about 62.5% of a yellow oil is separated,  $D^{15}$  0.9180,  $n_D$  - 78.8°, acid number 3.14, ester number 0.

*Red-fir oil*, obtained from the fresh needles and young twigs of small trees of *Pinus Douglasii taxifolia*, is a yellowish-green substance (yield 0.8—1%) having an odour resembling limonene;  $D^{23}$  0.8680,  $n_D$  - 62.5°, acid number 0, saponification number 86.6, after acetylation 92.1, free borneol content 27.18%. This oil contains no aldehyde, and the lower fractions give no nitrosochloride; the major fraction, b. p. 161—169°, contains camphene (*Pharm. Rev.*, 1908, 26, 326).

*African Elemi oil* is pale yellow to yellowish-green and moderately viscous. One sample gave 0.6% ash, acid number 55.3, saponification value 71.9, and the yield of ethereal oil was 8.1%, which contained considerable quantities of phellandrene, and had  $D^{15}$  0.8686,  $n_D$  + 50.5°. A second sample gave 0.53% ash, acid number 37.8, saponification value 46.2, and contained 4.4% of ethereal oil. A sample of *Uganda Elemi oil* from *Canarium Schweinfurthii* was colourless to pale yellow; it contained 0.3% ash, and had acid number 29.4, saponification value 44.8, and when steam distilled gave 11.2% of a pale yellow oil having  $D^{15}$  0.8451,  $n_D$  + 79.33°, and contained much phellandrene (*Bull. Imp. Inst.*, 1908, 6, 252).

*Lemon oil* from Messina is found to begin to boil at 175° and have the following limiting values,  $D^{15}$  0.856 to 0.861, the rotation varies somewhat with the district and ripeness of the fruit, but lies between +58° and +66° at 20°, citral content 4 to 7.5%. *Bergamot oil* from Messina has the limiting values  $D^{15}$  0.880 to 0.887,  $n_D$  + 7° to +25°, acid content calculated as acetic acid 0.15 to 0.2%, and with old oil up to 0.4%; ester content 33 to 44%, commences to boil at 180° or 72°/20 mm. (Berté and Romeo, Messina). *Sweet orange oil* from Messina (compare Abstr., 1907, i, 66) has the following limiting values,  $D^{15}$  0.847 to 0.852,  $n_D^{20}$  + 96° to 98°,  $n_D$  of the first 50% of distillate should be at least 1.5° higher than that of the

original oil, b. p.  $176^{\circ}$  to  $177^{\circ}$  or  $79^{\circ}$  to  $81^{\circ}/20$  mm. *Bitter orange oil*,  $D^{15}$  0.852 to 0.856,  $\alpha_D^{20} + 88^{\circ}$  to  $96^{\circ}$ , and  $\alpha_D$  of the first 50% of distillate should be at least  $3^{\circ}$  higher than that of the original oil. *Mandarin oil*,  $D^{15}$  0.854 to 0.858,  $\alpha_D + 67^{\circ}$  to  $73^{\circ}$ , and  $\alpha_D$  of first 50% should average  $3^{\circ}$  higher than that of the original oil.

A sample of *Eucalyptus oil* distilled in Java had  $D^{25}$  0.996,  $\alpha_D + 4.3^{\circ}$ , and commenced to boil at  $150$ — $200^{\circ}$ , when 77% distilled;  $200$ — $240^{\circ}$ , 16% distilled over; it appears to consist chiefly of cineol. Two other samples from Java: (I) (probably from *E. crebra*) contained little cineol, some phellandrene and cuminaldehyde; the constants are  $D^{15}$  0.9036,  $\alpha_D - 20.93^{\circ}$ . (II) (Probably from *E. piperita*) was a golden-yellow oil having  $D^{15}$  0.8974,  $\alpha_D - 28.43^{\circ}$ , and contained scarcely any cineol, but cuminaldehyde and a considerable quantity of phellandrene (*Jar. Land. Neder. Ind.*, 1907, 66). Oil from South Africa had  $D^{15.5}$  0.9227,  $\alpha_D + 3^{\circ}17'$ , and contained a considerable quantity of cineol, but no phellandrene.

*Pine oil (Oleum templinum)* has been definitely shown to contain borneol; the constants given for this oil are  $D^{15}$  0.8556,  $n_D^{20}$  1.47246,  $\alpha_D - 76.5^{\circ}$ , ester number 5.3. Freed from terpene and saponified, the alcohols obtained had b. p.  $190$ — $225^{\circ}$ ; the chief product had b. p.  $205$ — $215^{\circ}$ , and consisted chiefly of borneol. In addition to this constituent an alcohol of b. p.  $190$ — $197^{\circ}$ ,  $D^{15}$  0.9013, is present together with a sesquiterpene. *Siberian pine oil*, after heating with sulphuric acid and acetic acid to  $60^{\circ}$  and then saponifying with alcoholic potash, yields solid inactive camphene (compare *Chem. Zeit.*, 1908, 32, 922). *Australian pine-needle oil* from *Callitris glauca*, yield 0.6%, contains 12—16% bornyl acetate and geranyl acetate: by distilling the wood; a thick oil was obtained which contained a new phenol, *callitrol*.

Methyl sulphide has been detected in Réunion *Geranium oil* and also in African *geranium oil*. The sample of *Cochin wood oil* examined was brown with a green fluorescence; it had  $D^{15}$  0.9633,  $\alpha_D - 37.5^{\circ}$ ,  $n_D^{20}$  1.51236, acid number 7.8, ester number, 2.9. When steam-distilled, 69.9% of a lemon-yellow oil was obtained, having  $D^{15}$  0.9248,  $\alpha_D - 61.8^{\circ}$ ,  $n_D^{20}$  1.50252. Acid number 0, ester number 1.6. *Japanese star anise oil*, from *Illicium religiosum*, differs from the Chinese oil by not containing anethole and only a small quantity of safrole; it also contains cineol and probably linalool. The constants found were  $D^{15}$  0.9848,  $\alpha_D - 0.8^{\circ}$ , acid number 1.8, ester number 12.9.

*Kobuschi oil*, from young twigs of Japanese plants, differs from the oil previously described (*Abstr.*, 1908, i, 666); it was pale yellow with an odour of citral,  $D^{15}$  0.892,  $\alpha_D + 6.13^{\circ}$ , acid number 4.3, saponification value 19.1, after acetylation 56.48. It contained chiefly methylchavicol, together with citral, eugenol, and cineol. *Curled mint oil*, from the dry Hungarian plant, is similar in composition to the American and German product, but differs therefrom by its high carvone content, 72%, and its greater solubility. *Lovage root oil*—two fresh samples were examined: (I) one year roots, yield 0.22%,  $D^{15}$  1.0310,  $\alpha_D + 1.5^{\circ}$ ,  $n_D^{20}$  1.55148, acid number 5.8, ester number 223.5. (II) Two year roots, yield 0.55%,  $D^{15}$  1.0326,  $\alpha_D + 0.75^{\circ}$ ,  $n_D$  1.54944, acid number 6.1, ester number 224.5, after acetylation 227.8. *Linulos oil*, when saponified and steam distilled, yields an unusually light oil,  $D^{15}$  0.7727,

$\alpha_D + 1.75^\circ$ , b. p.  $42^\circ/18$  mm. This oil apparently contains isomeric octylenes and nonylenes, and an olefine of the formula  $C_{10}H_{16}$  probably myrcene.

*Matico oil*, from the leaves of *Piper mandoni*, yields about 0.8% of a brown, balsam-smelling oil,  $D^{15}_D 0.9360$ ,  $\alpha_D + 1.08^\circ$ ,  $n^{20}_D 1.49704$ , acid number 1.8, ester number 5.1, after acetylation 46.7 (*Pharm. Zentralh.*, 1908, 49, 974). Two samples of *Myrtle oil* from Corsica have been examined:  $D^{15}_D 0.8828$  and  $0.8868$ ,  $\alpha_D 26.75^\circ$  and  $23.25^\circ$ ,  $n^{20}_D 1.46644$  and  $1.46911$ , acid number 1.0 and 1.6, ester number 13.0 and 17.1, after acetylation 30.2 and 38.5. Two samples from *Syria* had  $D^{15}_D 0.8930$  and  $0.8985$ ,  $\alpha_D + 14.5^\circ$  and  $+ 11^\circ$ ,  $n^{20}_D -$  and  $1.46417$ , acid number 1.9 and —, ester number 20.3 and 26.6, after acetylation 72.0 and 70.7. One sample from *Asia Minor* had  $D^{15}_D 0.9138$ ,  $\alpha_D + 10.7^\circ$ ,  $n^{20}_D 1.46704$ , acid number 1.5, ester number 39.4, after acetylation, 94.9. Two samples of *Sage oil* from Corfu were found to have a different odour from the oil obtained from *Salvia officinalis* (this vol., i, 39); they were almost colourless, and had respectively  $D^{15}_D 0.9153$  and  $0.9132$ ,  $\alpha_D - 15.25^\circ$  and  $- 15.08^\circ$ , acid number 0.5 and 0.5, ester number 9.0 and 10.6. *Mexican Schinus oil*, differing from that previously described (*Abstr.*, 1908, i, 666), has been studied; it was pale yellow, having  $D^{15}_D 0.8492$ ,  $\alpha_D + 56.45^\circ$ ,  $n^{20}_D 1.47616$ , and contained a considerable quantity of phellandrene. *Canadian Snake root oil*, from *Asarum canadense* (compare *Abstr.*, 1908, i, 666), had the following constants: (I) Roots with fibre,  $D^{15}_D 0.9519$ ,  $\alpha_D - 10.5^\circ$ ,  $n^{20}_D 1.49987$ , acid number 4.7, ester number 74.7, after acetylation 125.0. (II) Roots without fibre,  $D^{15}_D 0.9520$ ,  $\alpha_D - 10.7^\circ$ ,  $n^{20}_D 1.48863$ , acid number 3.1, ester number 86.1, after acetylation 125.8. Flowers of *Tagetes patula* (*loc. cit.*) when fresh yield 0.08%, when dried 0.57%, of a brownish-yellow oil having  $D^{15}_D 0.8925$ ,  $\alpha_D - 9^\circ$ ,  $n^{20}_D 1.49938$ , acid number 6.4, ester number 10.6. The stalks and leaves when fresh or dry give 0.07% or 0.218% of a similar oil, having  $D^{15}_D 0.9034$ ,  $\alpha_D + 1.25^\circ$ ,  $n^{20}_D 1.49938$ , acid number 14, ester number 12.4. Further data for *Tetranthra oil* are given: (I) from the bark,  $D^{15}_D 0.9062$ ,  $\alpha_D + 14^\circ$ ,  $n^{20}_D 1.46595$ , ester number after acetylation 230.2; (II) from the leaves,  $D^{15}_D 0.8990$ ,  $\alpha_D - 12^\circ$ ,  $n^{20}_D 1.46426$ ; (III) from the fruit,  $D^{15}_D 0.8932$ ,  $\alpha_D + 6.13^\circ$ ,  $n^{20}_D 1.48141$ , and an aldehyde content of 85%. *Red cedar oil*, from dried leaves of *Thuja plicata* (*loc. cit.*), yield 1.32%, is pale yellow with a pungent thujone odour,  $D^{15}_D 0.9056$ ,  $\alpha_D + 5.07^\circ$ ,  $n^{20}_D 1.45721$ , acid number 0.8, ester number 16.9.

The following are described for the first time. *Oil of Barosma pulchellum*, obtained from the leaves, yield 3% of a golden-yellow oil with a decided unpleasant odour. It had  $D^{15}_D 0.8830$ ,  $\alpha_D + 8.51^\circ$ ,  $n^{20}_D 1.45771$ , acid number 18.5, ester number 27.2, after acetylation 237.0. The unpleasant smelling constituent is a pungent narcotic base, which has b. p.  $130-140^\circ/5$  mm., and in addition this oil contains citronellal and methylheptenone. *Oil from Satureja macrostema* is a pale yellow substance having an odour resembling mint, and  $D^{15}_D 0.9182$ ,  $\alpha_D + 6.85^\circ$ ,  $n^{20}_D 1.46852$ , acid number 15.6, ester number 10.3, after acetylation 37.9, soluble in all proportions of 90% alcohol. *Oil from Mexican Marsh Cypress (Taxodium mexicanum)* is light brown, odour resembling turpentine oil,  $D^{15}_D 0.8685$ ,  $\alpha_D - 10.33^\circ$ ,

$n_D^{20}$  1.46931, acid number 0.5, ester number 5.7. *Oil of Artemisia Herba-alba*, var. *densiflora* Bois (*Chieh Oil*) from Egypt.—The plant was steam distilled and gave 1.6% yield of a yellow oil possessing a decided thujone odour,  $D^{15}$  0.9192,  $\alpha_D$   $-5.33^\circ$ ,  $n_D^{20}$  1.45611, acid number 1.5, ester number 11.0, after acetylation 40.7 (compare Abstr., 1904, i, 605). J. V. E.

**Solubility of Kauri Copal.** CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1909, [iv], 5, 289—296).—Four grades of Kauri copal are recognised commercially, for which the author gives the following data:

	Kauri blonde.	Kauri brune.	Kauri busch.	Kauri busch récolté.
D .....	1.036/17°	1.053/9°	1.030/17°	1.038/15°
M. p. ....	165°	185°	150°	125°
	(softening at 175°)	(softening at 90°)	(softening at 60°)	(softening at 50°)
Acid number .....	70.9	78.8	83.1	81.8
Köttstorfer's index ...	73.0	89.7	78.5	87.0

The following table gives the % of matter insoluble in the boiling solvent:

Ethyl alcohol .....	6.60	35.80	12.30	4.20
Methyl „ .....	46.90	61.90	47.30	34.20
Amyl „ .....	0.0	0.0	0.0	0.0
Ether .....	61.80	60.70	55.10	51.10
Chloroform .....	54.40	58.70	50.70	43.40
Benzene .....	66.70	70.60	61.70	57.60
Acetone .....	8.90	38.70	20.70	11.30
Turpentine .....	77.50	73.60	72.90	63.0
Benzaldehyde .....	0.0	0.0	0.0	0.0
Aniline .....	0.0	0.0	0.0	0.0
Amyl acetate .....	0.0	2.0	0.0	0.0
Carbon tetrachloride...	81.10	77.3	71.90	63.0

C. S.

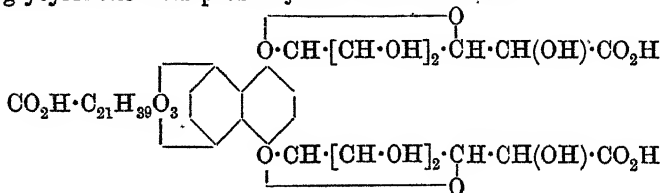
**A Liquid Resin.** WILHELM FAHRION (*Zeitsch. angew. Chem.*, 1909, 22, 582—583).—A liquid resin, *Tall oil*, has been obtained by Larsson as a by-product in the preparation of cellulose from Swedish pine wood by the soda process (*Svensk. Kem. Tidskr.*, 1905, 148). It is a dark brown, limpid liquid, and does not solidify at  $-20^\circ$ . It has b. p.  $270^\circ/40$  mm.,  $D^{15}$  0.997, acid number 163, iodine number 118, and hydrolysis number 179. The oil contains neutral substances, and when its alcoholic solution is neutralised, a precipitate is formed. These neutral substances are removed when the solution in 50% aqueous alcohol is shaken with light petroleum. The amount of such neutral substance is 9.4%, and on treatment with alcoholic potassium hydroxide a portion is hydrolysed to acids, but the greater portion cannot be hydrolysed. The composition of the resin is:—resin acids 85.2, oxy-acids 4.6, hydrolysable neutral compounds 2.9, non-hydrolysable 6.5%.

Whereas the abietic acids of ordinary colophony cannot be esterified by means of alcohol and sulphuric acid, it is shown that certain of the acids of tall oil are readily esterified. A liquid ester,  $C_{19}H_{29} \cdot CO_2Et$ ,

has been obtained with a hydrolytic number 186·7, instead of 169·7. The resin acid obtained from this ester is also liquid, and has a molecular weight 312·5. The acids which are not esterified are solid; they correspond exactly with a pale colophony, and give the Storch-Morawski reaction.

J. J. S.

**Glycyrrhizin.** ALEXANDER TSCHIRCH and S. GAUCHMANN (*Arch. Pharm.*, 1909, 247, 121—123. Compare Abstr., 1908, i, 898; Tschirch and Cederberg, Abstr., 1907, i, 545).—The formation of naphthalene when glycyrrhizic acid is distilled with zinc dust has been proved definitely. It is also found that phthalic acid is produced when glycyrrhizic acid is oxidised with potassium permanganate. From these results, and those obtained previously, the conclusion is drawn that glycyrrhizic acid probably has the constitution:



W. H. G.

**Sicilian Aloes.** G. CONDO-VISSICCHIO (*Arch. Pharm.*, 1909, 247, 81—95).—The native aloes of Sicily belong to the species *Aloe vulgaris*, and contain a hitherto unknown aloin, which it is proposed to designate *sicaloin*. It is considered probable, therefore, that the different properties of many of the aloins are due, not only to the different methods of preparation of the drug, but also to the conditions under which the plant grows. The sap of the Sicilian aloes does not contain emodin, but this substance is formed slowly when the sap is exposed to the air; the change is probably brought about by the action of oxydases.

*Sicaloin*,  $\text{C}_{15}\text{H}_{20}\text{O}_7 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , crystallises in white prisms; it loses  $1\text{H}_2\text{O}$  over sulphuric acid, decomposes slowly at  $110^\circ$ , and does not give Schonteten's or Bornträger's reaction. Estimations by Zeisel's method show that the molecule of *sicaloin* contains one methoxy-group.

W. H. G.

**Picrotoxin.** FRANCESCO ANGELICO (*Gazzetta*, 1909, 39, i, 296—303. Compare Abstr., 1907, i, 332).—Bromopicrotoxinin and the corresponding acid are stable towards permanganate, whilst picrotoxinin yields a complex mixture.

The oxidation of the acid obtained by oxidising bromopicrotoxin with permanganate with a boiling solution of chromic acid leads to the formation of *bromopicrotoxic acid*,  $\text{C}_{15}\text{H}_{15}\text{O}_7\text{Br} \cdot \frac{1}{2}\text{H}_2\text{O}$ , m. p.  $180^\circ$  (decomp.),  $[\alpha]_D^{25} -96\cdot38^\circ$ . Alkalis convert it into a mixture of products, a solution of which gives the reactions of an aromatic *o*-dihydroxy-derivative. When baryta water is used, two substances may be isolated. One of these crystallises from water in small, white

needles, m. p.  $250^{\circ}$ , and has the composition  $C_{14}H_{15}O_7Br$ . It may be called *bromopicrotoxinic acid*. The second product is *hydroxypicrotoxinic acid*,  $C_{14}H_{15}O_7 \cdot OH$ , forming large, white prisms, m. p.  $270^{\circ}$  (decomp.).

Cold saturated barium hydroxide solution converts picrotoxinin into a *barium salt*,  $C_{13}H_{16}O_7Ba$ , the acid from which has only been obtained in an oily form.

The oxidation products of picrotin contain two acids,  $\alpha$ -*picrotinic*, m. p.  $245^{\circ}$  (decomp.), not yet analysed, and  $\beta$ -*picrotinic*,  $C_{11}H_{14}O_5$ , white leaflets, m. p.  $254^{\circ}$ , subliming unchanged at  $330^{\circ}$ . The *acetyl* derivative forms white crystals, m. p.  $220^{\circ}$ . C. H. D.

**Bile Pigments: Bilirubin, Biliverdin, and their Fission Products.** WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1909, 59, 63—95).—Bilirubin has the formula  $C_{32}H_{36}O_6N_4$ . Under certain definite conditions it is transformed into a green colouring matter of the composition  $(C_{16}H_{18}O_4N_2)_x$ , soluble in alcohol (biliverdin), but in the presence of excess of an alkali carbonate and atmospheric oxygen it is, in part, decomposed further, even at  $10^{\circ}$ , and ether-soluble acids, including hæmatic acid, are formed. By warming with sodium hydroxide, especially when a little oxygen (one atomic proportion) is supplied by an oxidising agent, 40% of the pigment is transformed into ether-soluble acids, half being hæmatic acid; this behaviour is very different from that of hæmatin, which is stable under the conditions mentioned. A relationship between bilirubin and the indigoid colouring matters prepared by Friedländer, is suggested. G. B.

**Studies in the Coumaran Group. II.** STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1909, 42, 901—910. Compare Abstr., 1908, i, 442).—Ethyl chloroacetate reacts as easily with orcinol as with resorcinol (compare Hantzsch, Abstr., 1887, 282) in the presence of sodium ethoxide to form *ethyl 5-hydroxy-2:3-dimethylcoumarilate*,  $OH \cdot C_6H_2Me \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CMe \end{smallmatrix} C \cdot CO_2Et$ , which crystallises in white needles, m. p.  $212^{\circ}$ . This constitution is held to be the more probable, although it might be the 2:5-dimethylcoumarilate. This ester, on methylation with methyl sulphate and potassium hydroxide, yields *ethyl 5-methoxy-2:3-dimethylcoumarilate*,  $C_{14}H_{16}O_4$ , which crystallises from alcohol in needles, m. p.  $115-116^{\circ}$ , and, on hydrolysis with potassium hydroxide, yields *5-methoxy-2:3-dimethylcoumarilic acid*,  $C_{12}H_{12}O_4$ , forming white needles, m. p.  $215^{\circ}$  (decomp.); its *potassium salt* is difficultly soluble.

When the acid is heated in a retort, there is a vigorous evolution of carbon dioxide, and the corresponding coumarone distils over; it can be freed from any unchanged acid by distillation in a current of steam.

*5-Methoxy-2:3-dimethylcoumarone*,  $OMe \cdot C_6H_2Me \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CMe \end{smallmatrix} CH$ , crystallises from dilute alcohol in glistening, white leaflets, m. p.  $61-62^{\circ}$ .

Præonol and ethyl bromoacetate in the presence of sodium ethoxide condense after twelve hours' heating at  $100^{\circ}$  to form *ethyl 2-acetyl-5-methoxyphenoxyacetate*,  $OMe \cdot C_6H_3Ac \cdot O \cdot CH_2 \cdot CO_2Et$ , which forms leaflets, m. p.  $78^{\circ}$ . The *acid*,  $C_{11}H_{12}O_5$ ,  $H_2O$ , prepared by hydrolysing the

mixture from the phenol and ethyl bromoacetate reaction, forms stout crystals, m. p. 132°. On digestion of this acid with acetic anhydride and sodium acetate, a good yield of 5-methoxy-2-methylcoumarone (*loc. cit.*) is obtained. This method, due to Rössing (Abstr., 1885, 388), is a general one, and has been used frequently in this work.

2-Acetyl-5-ethoxyphenoxyacetic acid,  $C_{12}H_{14}O_5$ , prepared from ethyl ether of resacetophenone and ethyl bromoacetate, forms crystals, m. p. 150°, and the 5-ethoxy-2-methylcoumarone,  $C_{11}H_{12}O_3$ , prepared from it by the acetic anhydride method forms leaflets, m. p. 51—52°, b. p. 255°/719 mm.

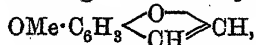
2-Propionyl-5-ethoxyphenoxyacetic acid,  $C_{13}H_{16}O_5$ , from the ethyl ether of propionylresorcinol, forms white needles, m. p. 125—126°, and the 5-ethoxy-2-ethylcoumarone,  $C_{12}H_{14}O_3$ , derived from it crystallises in white leaflets, m. p. 66—67°.

Condensation of ethyl bromoacetate and 2-acetyl-1-naphthol leads to the formation of 2-acetyl-1-naphthoxyacetic acid,  $C_{14}H_{12}O_4$ , which separates from alcohol in leaflets, m. p. 130°. The acetic anhydride method is a particularly good one for the preparation of 2-methyl- $\alpha$ -naphthafuran (compare Stoermer, Abstr., 1900, i, 654).

Condensation of ethyl chloroacetate and phloroglucinol and subsequent methylation gives a poor yield of ethyl 3:5-dimethoxy-2-methyl-

coumarilate,  $C_6H_2(OMe)_2 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown OMe \diagup \end{smallmatrix} C \cdot CO_2Et$ . It is much better to use the dimethyl ether of phloroacetophenone and ethyl bromoacetate. It crystallises in white needles, m. p. 133—134°. The acid,  $C_{12}H_{12}O_5$ , obtained by the hydrolysis of the ester by alcoholic potassium hydroxide forms rosettes of needles from alcohol, m. p. 242° (decomp.). 3:5-Dimethoxy-2-methylcoumarone,  $C_{11}H_{12}O_3$ , forms prisms, m. p. 39°, b. p. 283°/714 mm. Unlike 5-methoxy-2-methylcoumarone, it is odourless; successful reduction to the corresponding coumaran has not yet been accomplished. W. R.

**Coumarone Group.** H. DUMONT and STANISLAUS VON KOSTANECKI (*Ber.*, 1909, 42, 911—915. Compare preceding abstract).—Condensation of *p*-methoxysalicylaldehyde and ethyl bromoacetate in the presence of sodium ethoxide gives ethyl 5-methoxy-2-aldehydophenoxyacetate,  $OMe \cdot C_6H_3(CHO) \cdot O \cdot CH_2 \cdot CO_2Et$ , which crystallises from dilute alcohol in silky needles, m. p. 68—69°. The free acid,  $C_{10}H_{10}O_5$ , crystallises in needles, m. p. 144°, and on treatment with acetic anhydride and sodium acetate gives 5-methoxycoumarone,



in good yield. It is a colourless oil, b. p. 226°/706 mm., and has an odour resembling *o*-hydroxyacetophenone.

*p*-Ethoxysalicylaldehyde,  $C_9H_{10}O_3$ , prepared from resorcydaldehyde, potassium hydroxide, and ethyl iodide, forms long, white needles, m. p. 35°. It yields the following compounds: 5-ethoxy-2-aldehydophenoxyacetic acid,  $C_{11}H_{12}O_5$ , crystallising in needles from alcohol, m. p. 189°; its ethyl ester,  $C_{13}H_{16}O_5$ , glistening leaflets, m. p. 90°; and 5-ethoxycoumarone,  $C_{10}H_{10}O_3$ , leaflets, m. p. 10°, b. p. 238°/700 mm.

W. R.

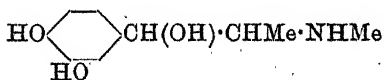
**Action of Aluminium Chloride on Diphenyl Disulphide and the Thiocresols, and the Action of Sulphuric Acid on Thianthren.** J. J. B. DEUSS (*Rec. trav. chim.*, 1909, 28, 136—141).—When diphenyl disulphide dissolved in dry light petroleum is treated with aluminium chloride and the product heated to boiling for several hours, hydrogen chloride and sulphide are evolved, and about 50% of the theoretical quantity of thianthren together with some thiophenol are formed. Thus a better yield of thianthren is obtained than when thiophenol is used (compare Abstr., 1908, i, 530). On similarly treating light petroleum solutions of *o*- and *p*-thiocresols, prepared from the toluidines by Bourgeois' method (Abstr., 1900, i, 163), with aluminium chloride, hydrogen sulphide is evolved and the corresponding ditolyl sulphides are produced. *m*-Thiocresol is not attacked, and in no case could a methylthianthren be obtained. The difference in the behaviour of *m*-thiocresol from that of the ortho- and para-compounds is probably to be explained by the formation of an additive compound of aluminium chloride with the former compound (compare Boeseken, Abstr., 1905, i, 424). In fact, when finely powdered aluminium chloride is added to a solution of *o*- or *p*-thiocresol in carbon disulphide, the thiocresol is recovered unchanged on evaporation of the solvent, whilst with *m*-thiocresol a homogeneous, black residue is obtained, having the composition  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SH}\cdot\text{AlCl}_3$ .

Genvresse (Abstr., 1897, i, 240, 514), by treating thianthren with sulphuric acid containing 30% of sulphur trioxide, obtained a red colouring matter. The latter is better prepared by heating thianthren on a water-bath for eight days (and nights) with ordinary sulphuric acid. The colouring matter is soluble in dilute sulphuric acid, but precipitated by barium carbonate. A small quantity of *thianthren-disulphonic acid*,  $\text{C}_{12}\text{H}_6\text{S}_2(\text{SO}_3\text{H})_2$ , is also formed, of which the *potassium* salt forms white, crystalline crusts. The latter when treated with phosphorus pentachloride gives an insoluble product.

During the course of the sulphonation, a sublimate of Krafft and Lyons' thianthren disulphoxide is produced on the neck of the flask.

E. H.

**Syntheses in the Adrenaline Series.** CARL MANNICH and JACOBSON (*Chem. Zentr.*, 1909, i, 923—924; from *Apoth. Zeit.*, 1909, 24, 60—61).—By manipulative improvements on the method employed by Barger and Jowett (*Trans.*, 1905, 87, 967) and by Pauly and Neukam (this vol., i, 96), the authors have obtained the pure methylene ether of adrenaline, m. p. 81°, b. p. 189—192°/14 mm., and also *adrenaline dimethyl ether*, m. p. 64—65°; the *hydrochloride* of the latter base has m. p. 178—179°. By the addition of two bromine atoms to methylisoeugenole and subsequent replacement of one bromine atom, the bromohydrin,  $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}(\text{OH})\cdot\text{CHMeBr}$ , m. p. 78°, is



obtained, which, with methylamine, yields  *$\beta$ -methyladrenaline dimethyl ether*, m. p. 63°. By boiling with hydriodic acid, this was converted into  *$\beta$ -methyladrenaline* (annexed formula), of which the

*hydriodide* has m. p. 160°. According to Kobert the last-named base has not the physiological action of adrenaline (compare Büttcher, this vol., i, 152).

G. B.

**Ephedrine and  $\psi$ -Ephedrine.** ERNST SCHMIDT (*Arch. Pharm.*, 1909, 247, 141—149. Compare Abstr., 1908, i, 452).—An investigation on the preparation and properties of substances of the types:  $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NMe}_3\text{Cl}$  and  $\text{NMe}_3\text{Cl}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{OH}$ ; the two compounds formulated should yield ephedrine and  $\psi$ -ephedrine on the elimination of methyl chloride.

[With A. GOEHRING.]— $\beta$ -Bromopropiophenone unites with pyridine, forming an *additive* product,  $\text{COPh}\cdot\text{CHMe}\cdot\text{C}_5\text{NH}_5\text{Br}$ , which crystallises in colourless prisms, m. p. 130—131°; the *platinichloride*,  $(\text{C}_{14}\text{H}_{14}\text{ON})_2\text{PtCl}_6$ , forms yellowish-red needles, m. p. 222—223°; the *aurichloride*,  $(\text{C}_{14}\text{H}_{14}\text{ON})\text{AuCl}_4$ , forms stellate groups of yellow needles, m. p. 134—136°; the *picrate* crystallises in yellow needles, m. p. 134—136°.

Trimethylamine and  $\beta$ -bromopropiophenone combine to form the *additive* product,  $\text{COPh}\cdot\text{CHMe}\cdot\text{NMe}_3\text{Br}\cdot\text{H}_2\text{O}$ , crystallising in colourless prisms, m. p. 206—208° (dried in a desiccator), 212—213° (dried in a steam-oven); the *platinichloride*,  $(\text{C}_{12}\text{H}_{13}\text{ON})_2\text{PtCl}_6$ , forms reddish-yellow needles, m. p. 231°; the *aurichloride* crystallises in yellow leaflets, m. p. 156°. The *additive* product when reduced with sodium amalgam does not yield the corresponding secondary alcohol, but a *substance*, which crystallises in slender, white needles, m. p. 150—151°.

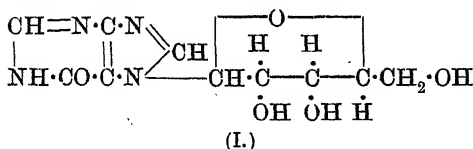
Phenylethylcarbinol, when acted on by bromine in acetic acid, yields a *dibromo-derivative*,  $\text{C}_9\text{H}_{10}\text{OBr}_2$ , which crystallises in aggregates of colourless needles, m. p. 68—69°. The *oily product*, obtained at the same time as the *dibromo-derivative*, is converted by trimethylamine into an *additive* product, which, after treatment with silver chloride, yields the *platinichloride*,  $[\text{OH}\cdot\text{CHPh}\cdot\text{C}_2\text{H}_4\cdot\text{NMe}_3]_2\text{PtCl}_6$ , opaque, nodular crystals, m. p. 215°, and transparent, hexagonal prisms, m. p. 218°; the *aurichloride*,  $(\text{C}_{12}\text{H}_{20}\text{ON})\text{AuCl}_4$ , forms glistening leaflets and slender needles.

[With G. BÜMMING.]—Both ephedrine hydrochloride and  $\psi$ -ephedrine hydrochloride, when distilled in a stream of carbon dioxide, yield methylamine hydrochloride and propiophenone, and in the latter case also ammonium chloride. It is therefore probable that the hydroxyl group in ephedrine and  $\psi$ -ephedrine is connected with a carbon atom adjoining a phenyl group.

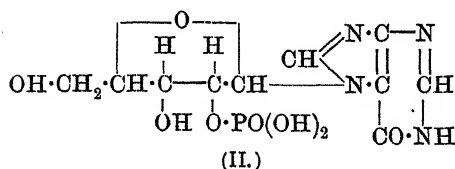
W. H. G.

**Carnine and Inosic Acid. II.** FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1909, 30, 147—164. Compare Abstr., 1908, i, 561; Neuberg and Brahn, Abstr., 1907, i, 1097; 1908, i, 1029; Bauer, Abstr., 1907, i, 1098; Levene and Jacobs, Abstr., 1908, i, 931).—Attempts to crystallise the pentose obtained from inosine have been unsuccessful; the syrup has  $[\alpha]_D^{25} - 19.6^\circ$  in aqueous solution. It is considered probable that the sugar is *d*-lyxose, although con-

firmation of this is still lacking. Assuming *d*-lyxose to be present in inosine, then the latter substance probably has formula (I).

$$\begin{array}{c} \text{CH}=\text{N}\cdot\text{C}\cdot\text{N} \\ | \qquad \qquad || \\ \text{H} \qquad \qquad \text{H} \end{array} \begin{array}{c} \diagup \\ \text{CH} \end{array} \begin{array}{c} \text{O} \\ | \\ \text{H} \quad \text{H} \end{array}$$


following reasons: (1) a pentose-phosphoric acid resulting from the combination of phosphoric acid with a sugar through the aldehyde

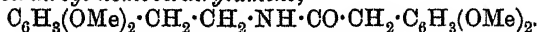


xanthine base is not joined directly with the phosphoric acid.

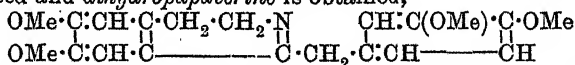
On the assumption that inosic acid contains *d*-lyxose, it is probable that inosic acid has the constitution represented by formula (II).

W. H. G.

**Complete Synthesis of Laudanosine.** AMÉ PICTET and MLLÉ. M. FINKELSTEIN (*Compt. rend.*, 1909, 148, 925—927. Compare Abstr., 1900, i, 685).—The first complete synthesis of an opium alkaloid has been effected by the following operations: (1) Methylvanillin is converted into dimethylhydrocaffeic acid (Tiemann, Abstr., 1878, 580); the amide of this acid on treatment with sodium hypobromite yields *homoveratrylamine*,  $C_6H_3(OMe)_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$ . (2) *Homoveratroyl chloride*,  $C_6H_3(OMe)_2 \cdot CH_2 \cdot COCl$ , is prepared from Tiemann's homoveratric acid (Abstr., 1878, 503). (3) In the presence of sodium hydroxide, homoveratrylamine and homoveratroyl chloride react to give *homoveratroyl homoveratrylamine*.



(4) When this is treated with phosphoric oxide, 1 mol.  $H_2O$  is eliminated and *dihydropapaverine* is obtained.

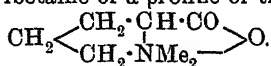


(5) Reduction of the *methochloride* of <sup>2</sup>this base leads to the formation of racemic *N*-methyltetrahydropapaverine, from which laudanone is prepared by the method described in a previous communication.

W. O. W.

**Stachydrine.** ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1909, 59, 233—235).—Stachydrine,  $C_7H_{13}O_2N$ , discovered by von Planta and Schulze in the tubers of *Stachys*, does not contain a double linking; on treatment with concentrated potassium hydroxide, dimethylamine is evolved. A carboxyl group is present. There appears to be a pyrrolidine ring, which is in agreement with the fact that on destructive distillation the vapours of stachydrine give the

pine-wood reaction for pyrrole. It is therefore suggested that the substance is a dimethylbetaine of  $\alpha$ -proline of the following structure :



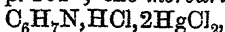
G. B.

**Bases Contained in the Tar from Otto-Hilgenstock Coke-Ovens.** FREDERICK GEORGE TROBRIDGE (*J. Soc. Chem. Ind.*, 1909, 28, 230—232).—Coke-oven tar yields a basic oil volatile in steam, 24% of which distils over below 170°, from which the following bases have been isolated: pyridine, 2-methylpyridine, 4-methylpyridine, and 2:4-dimethylpyridine.

Great discrepancies appear in the values recorded by various authors for the m. p.'s of the platinichlorides of these bases. It is found, as a general rule, that the platinichlorides, prepared by adding a solution of platinic chloride to an acidified aqueous solution of the hydrochloride of the base and evaporating, are darker in colour and have higher m. p.'s than those prepared in absolute alcoholic solution and crystallised by spontaneous evaporation. The compounds do not differ in chemical composition, and although they differ in crystalline habit, they nevertheless belong to the same crystallographic system. In some cases it is possible to convert one form into the other by recrystallisation from the different solvents. Pyridine aurichloride behaves in the same way, but the aurichlorides of the other bases give only slight indications of anything similar.

Pyridine platinichloride forms red crystals, m. p. 241—242°, and golden scales, m. p. 228°; the aurichloride forms golden-yellow crystals, m. p. 323°, and lemon-yellow crystals, m. p. 329°; the *picrate* forms canary-yellow needles, m. p. 163°.

2-Methylpyridine platinichloride crystallises in orange-red prisms, m. p. 194° (decomp.), and yellow scales, m. p. 178° (decomp.); the aurichloride forms bright yellow crystals, m. p. 175°; the *picrate* forms lemon-yellow needles, m. p. 161°; the *mercurichloride*,



crystallises in small plates or stout prisms, m. p. 151°.

4-Methylpyridine platinichloride forms red, rhombic crystals, m. p. 208°, and golden scales of the rhombic system, m. p. 208° (decomp.); the aurichloride crystallises from alcohol in bright yellow needles, m. p. 203°, and from water in bright yellow needles, m. p. 205°; the *picrate* forms small, pale lemon-yellow needles, m. p. 160°; the *mercurichloride* crystallises in slender needles, m. p. 121°. 2:4-Dimethylpyridine platinichloride forms orange-red, monoclinic crystals, m. p. 216° (decomp.), and minute prisms with pyramidal ends belonging to the monoclinic system, m. p. 209° (decomp.); the aurichloride forms yellow crystals, m. p. 77°; the *picrate* forms yellow crystals, m. p. 178°; the *mercurichloride*,  $\text{C}_7\text{H}_9\text{N}, \text{HCl}, 2\text{HgCl}_2$ , crystallises in white, hair-like needles, m. p. 128.5°.

W. H. G.

**Constitution of Conhydrine (Optically Active  $\alpha$ -Ethylpiperidylalkine).** KARL LÖFFLER and REINHOLD TSCHUNKE (*Ber.*, 1909, 42, 929—948).—The relationships of conhydrine to  $\beta$ -coniceine (2-allylpiperidine, this vol., i, 180) indicate that the former compound

must be either  $\alpha$ - or  $\beta$ -hydroxypropylpiperidine. It has been synthesised by the addition of hydrogen iodide to  $\beta$ -coniceine, replacement of the iodine by the acetoxy-group, and replacement of this latter by hydroxyl. Two active compounds are thus obtained, which can be separated by crystallisation from light petroleum, but neither is identical with conhydrine. This latter compound must therefore be  $\alpha$ -hydroxypropylpiperidine, as suggested by Engler and Bauer (Abstr., 1891, 1504; 1894, i, 471). This is confirmed by the fact that when water is eliminated from conhydrine by heating with fuming hydrochloric acid, the products include  $\gamma$ -coniceine, in addition to  $\alpha$ - and  $\beta$ -coniceines and *isoallyl*piperidine. The  $\gamma$ -coniceine is the product which forms a deliquescent hydrochloride; it has the constitutional formula  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CH}_2 \end{smallmatrix}\text{CH}_2$ , and is

also formed in small quantity by the action of phosphoric oxide on conhydrine. Engler and Bauer's inactive  $\alpha$ -hydroxypropylpiperidine also yields  $\gamma$ -coniceine when heated with phosphoric anhydride, whereas  $\beta$ -hydroxypropylpiperidine yields no trace of the  $\gamma$ -base. The formation of  $\gamma$ -coniceine from  $\alpha$ -hydroxypropylpiperidine can readily be explained by the formation of  $\text{C}_5\text{NH}_9\cdot\text{CH}\cdot\text{CH}_2\text{Me}$ , which undergoes molecular rearrangement by the shifting of the double linking.

\* The conclusion is drawn that  $\beta$ -coniceine and 2-*isoallyl*piperidine are *cis* or *trans* stereoisomerides, but that conhydrine and  $\psi$ -conhydrine are structurally different and not stereoisomeric, since the latter yields neither  $\beta$ - nor  $\gamma$ -coniceine when treated with phosphoric oxide.

Details for the separation of  $\beta$ -coniceine and the isomeric liquid base (2-*isoallyl*piperidine) (Abstr., 1905, i, 917) are given. The latter can be obtained pure by some twelve recrystallisations of the hydrochloride from acetone; it has the same m. p. as the dextro-compound obtained by resolving inactive *iso*-2-allylpiperidine with *d*-tartaric acid (this vol., i, 180). The base has  $D_{15}^{25} 0.8672$  and  $[\alpha]_D^{25} -29.02^\circ$ .

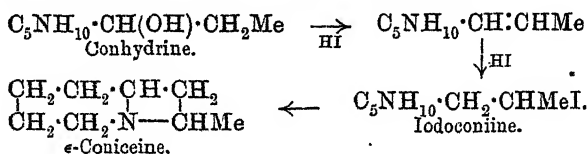
Both  $\beta$ -coniceine and its isomeride combine with hydrogen iodide when heated at  $100^\circ$  with fuming hydriodic acid and red phosphorus, yielding *iodoconiine hydriodide*,  $\text{C}_8\text{H}_{16}\text{NI}\cdot\text{HI}$ , in the form of compact needles, m. p.  $195\text{--}198^\circ$ . The same product is also formed by the action of hydriodic acid and red phosphorus on conhydrine at  $140\text{--}145^\circ$ .

Alkalis and moist silver oxide react with this iodine derivative, yielding the bicyclic conidine, but with silver acetate it yields an acetate from which 2- $\beta$ -hydroxypropylpiperidine is obtained by hydrolysis with potassium hydroxide solution. When this hydroxy-derivative is crystallised from light petroleum, it yields a pure product crystallising in large refracting plates, m. p.  $84\text{--}86^\circ$ , and with  $n_D +22.5^\circ$  in a 5-dcm. tube. The *hydrochloride* forms long needles, m. p.  $141\text{--}142^\circ$ ; the *aurichloride*, large plates, m. p.  $99^\circ$ , and the *platinichloride*, hyacinth-red prisms, m. p.  $111^\circ$ . The light petroleum mother liquors yield an isomeride which is laevorotatory, but which has not been obtained pure.

Hydrogen chloride also combines with  $\beta$ -conceine at  $100^\circ$ , yielding *chloroconine hydrochloride*,  $C_8H_{10}N \cdot CH_2 \cdot CHMeCl, HCl$ , which crystallises in brilliant needles, m. p.  $199^\circ$ ; the *platinichloride* forms long needles, m. p.  $210-211^\circ$ , but the *aurichloride* is an oil. The chloro-derivative reacts with alkalis in much the same manner as the iodo-derivative. When the acetate is boiled with potassium carbonate solution it yields a product melting at  $93-94^\circ$ , but its composition does not correspond with that of a mono- or di-acetyl derivative. Hydrolysis with potassium hydroxide solution gives rise to the hydroxy-compound, m. p.  $84-86^\circ$ , together with a considerable amount of the laborotatory isomeride.

It has been found possible by the addition to, and subsequent removal of hydrogen chloride from,  $\beta$ -conceine, or its stereoisomeride, partly to transform each into the other. A considerable amount of  $\gamma$ -conceine is formed by the elimination of water from conhydrine by means of fuming hydrochloric acid at  $200-220^\circ$ . It can be isolated in the form of the *cadmium salt*,  $C_8H_{15}N, HI, CdI_2$ , which crystallises from hot water in long needles, m. p.  $146-147^\circ$ . The *platinichloride* has m. p.  $192^\circ$ . J. J. S.

**Constitution and Synthesis of  $\epsilon$ -Conceine (2-Methylconidine and *iso*-2-Methylconidine).** KARL LÖFFLER (*Ber.*, 1909, 42, 948-960).—The  $\epsilon$ -conceine obtained by Lellmann (*Abstr.*, 1890, 1328) by the action of alkali on Hofmann's iodoconiine is shown to be a mixture of two stereoisomeric tertiary bases. The formation of these bases is represented by the following scheme:



The base contains two asymmetric carbon atoms, and the two isomerides isolated correspond with the  $(- -)$  and  $(- +)$  compounds.

The same stereoisomerides are formed by the action of hydrobromic or hydriodic acid on  $\alpha$ -pipecolylmethylalkine (2- $\beta$ -hydroxypropyl-piperidine). The dicyclic ring system shown above has been previously termed conidine (*Abstr.*, 1907, i, 437), and the two bases of which  $\epsilon$ -conceine is composed are called 2-methylconidine and *iso*-2-methylconidine respectively.

$\epsilon$ -Conceine is most readily obtained by the action of concentrated potassium hydroxide solution on bromoconiine (Löffler and Kirschner, *Abstr.*, 1905, i, 938). The yield is only some 20-25%, as considerable amounts of tarry matter are formed; the crude base is best isolated in the form of its picrate (m. p.  $220-221^\circ$ ). The base distils at  $150-153^\circ/748$  mm., and has  $D^{15} 0.8836$  and  $\alpha +42.34^\circ$ . It can be resolved into two components, 2-methylconidine and *iso*-2-methylconidine, by fractional crystallisation of the acid *d*-tartrate from water.

After repeated crystallisation, the *d*-tartrate of the *iso*-base, which is

sparingly soluble in water, is obtained as long, well-developed needles, containing  $2\text{H}_2\text{O}$ , and having m. p.  $91-92^\circ$ . *iso*-2-Methylconidine is a clear, strongly refracting liquid, b. p.  $143-145^\circ$ ,  $D_{15}^{25} 0.8624$ , and  $[\alpha]_D^{25} -87.34^\circ$ . It is a strong base absorbing carbon dioxide, and is stable towards permanganate. The *hydrochloride* is deliquescent; the *aurichloride*,  $\text{C}_8\text{H}_{15}\text{N} \cdot \text{HAuCl}_4$ , crystallises in yellow, feathery needles, m. p.  $198-199^\circ$ . The *platinichloride* forms similar needles, m. p.  $185^\circ$ . The *ethiodide*,  $\text{C}_8\text{H}_{15}\text{N} \cdot \text{EtI}$ , forms a snow-white powder, m. p.  $180-181^\circ$ . It also forms a sparingly soluble *picrate* and *mercurichloride*.

2-Methylconidine d-tartrate is more readily soluble in water, and crystallises in long, slender needles containing  $2\text{H}_2\text{O}$ , and has m. p.  $72-73^\circ$ . The base has b. p.  $151-154^\circ$ ,  $D_{15}^{25} 0.8856$ , and  $[\alpha]_D^{25} +67.4^\circ$ . The *platinichloride*,  $(\text{C}_8\text{H}_{15}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$ , forms nodular crystals, m. p.  $184-185^\circ$ . The *aurichloride* has m. p.  $167-168^\circ$ , and the *ethiodide* has m. p.  $165^\circ$  (decomp.). J. J. S.

*b*- $\psi$ -Conhydrine. KARL LÖFFLER (*Ber.*, 1909, 42, 960-962).—*b*- $\psi$ -Conhydrine (compare this vol., i, 181) is merely a monohydrate of  $\psi$ -conhydrine, and has the formula  $\text{C}_8\text{H}_{17}\text{ON} \cdot \text{H}_2\text{O}$ . When exposed to the air for some time, or over sulphuric acid, it loses its water and then has the m. p. of conhydrine ( $106^\circ$ ). The hydrate when plunged in a bath at  $58^\circ$  melts at  $58-60^\circ$ . J. J. S.

Derivatives of Piperazine. WILLEM A. VAN DORP, jun. (*Rec. trav. chim.*, 1909, 28, 68-91. Compare Franchimont, *Abstr.*, 1907, i, 395).—When piperazyldicarbamide dinitrate, prepared by mixing a hydrochloric acid solution of piperazine with a concentrated aqueous solution of potassium isocyanate and treating the aqueous solution of the resulting carbamide with nitric acid, is acted on with absolute nitric acid, almost equal volumes of carbon dioxide and nitrous oxide are evolved, the amino-groups being attacked and *piperazine dinitrate*, small, limpid, prismatic crystals, together with a small quantity of a second substance, possibly nitropiperazine, being formed. Dibenzene-sulphonpiperazide, obtained by the action of benzenesulphonyl chloride on piperazine, reacts with absolute nitric acid, giving *dinitropiperazine*,  $\text{CH}_2 \cdot \text{N}(\text{NO}_2) \cdot \text{CH}_2$ , which forms fine colourless needles, m. p.  $215^\circ$ , and on reduction gives Schmidt and Wichmann's piperazyldihydrazine (*Abstr.*, 1892, 210). Dinitropiperazine is not attacked by absolute nitric acid, consequently the formation of nitrous oxide by the action of nitric acid on piperazyldicarbamide dinitrate is not due to the decomposition of the former compound. The reaction is thus completely distinguished from the action of absolute nitric acid on piperyl-carbamide, which gives nitropiperidine.

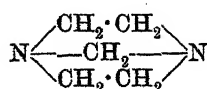
Ethyl piperazine-1 : 4-dicarboxylate, prepared by the action of ethyl chloroformate on piperazine in the presence of alkali, has m. p.  $45^\circ$  (Rosdalsky, *Abstr.*, 1896, i, 257, gives  $42^\circ$ ).

Methyl 1 : 4-piperazinedicarboxylate,  $\begin{array}{c} \text{CH}_2 \cdot \text{N}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{N}(\text{CO}_2\text{Me}) \cdot \text{CH}_2 \end{array}$ , obtained

similarly, forms large, colourless, transparent, cuspidated crystals, m. p.  $81^{\circ}$ . When either of these urethanes is dissolved in absolute nitric acid, oxidation occurs, giving very fine white needles of a substance, which was not further examined.

*Dipicrylpiperazine*,  $\text{CH}_2 \cdot \text{N}[\text{C}_6\text{H}_2(\text{NO}_2)_3] \cdot \text{CH}_2$ , resulting when piperazine is treated with picryl chloride, forms small, orange-yellow crystals, decomposing at about  $287^{\circ}$ . It dissolves in absolute nitric acid, undergoing slight oxidation, and gives an insoluble, amorphous, red substance.

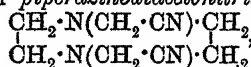
According to Rosdalsky (*loc. cit.*), the action of formaldehyde on a slight excess of piperazine gives methylenepiperazine (annexed formula), whilst



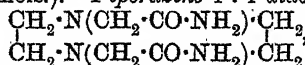
Herz (Abstr., 1897, i, 488), using excess of formaldehyde, obtained the compound  $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_2$ . Ladenburg and Herz, moreover, showed (Abstr., 1898, i, 209) that the product methylenepiperazine is decomposed by phenol, thus invalidating

Rosdalsky's molecular-weight determinations. The author, repeating Rosdalsky's experiments, obtained a compound with the empirical formula,  $\text{C}_5\text{H}_{10}\text{N}_2$ , in the presence of even a slight excess of aldehyde, however, the product seems to be identical with Herz's substance. Eschweiler having shown (Abstr., 1894, i, 267) that hydrogen cyanide

acts on hexamethylenetetramine, rupturing the  $\text{CH}_2$  groups, the action of this reagent on methylene-piperazine,  $\text{C}_5\text{H}_{10}\text{N}_2$ , was studied. The reaction of methylene piperazine with hydrogen cyanide gives small, limpid crystals of *piperazinediacetonitrile*,



m. p.  $165^{\circ}$ , of which a better yield is obtained by treating piperazine (1 mol.) in aqueous solution with formaldehyde (2 mols.) and then with hydrogen cyanide (2 mols.). *Piperazine-1:4-diacetamide*,



prepared by hydrolysing the nitrile with sulphuric acid, forms small crystals decomposing above  $250^{\circ}$ ; the *dihydrochloride* is formed by hydrolysis with hydrochloric acid. When the nitrile is boiled for a prolonged period with barium hydroxide solution, *piperazine-1:4-di-*

*acetic acid*,  $\text{CH}_2 \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H}) \cdot \text{CH}_2 + 2\text{H}_2\text{O}$ , is formed in magnificent,

colourless, transparent crystals, which effloresce in the air; the *barium*,

*silver*, *sodium*, and *potassium* salts were prepared. The acid forms an

additive compound,  $\text{C}_8\text{H}_{14}\text{O}_4\text{N}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{HCl}$ , with hydrogen chloride, which, when heated at  $100^{\circ}$ , loses water, but not hydrogen chloride; it is not decomposed by boiling water, from which it crystallises in brilliant, limpid crystals. An analogous compound is formed with nitric acid.

All attempts to esterify the acid failed. When an absolute alcoholic solution of piperazine (1 mol.) is treated with ethyl chloroacetate

(1 mol.), the product must contain ethyl piperazine-1:4-diacetate, since on saponification with baryta the acid is formed, but the ester could not be obtained pure.

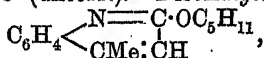
It is suggested, in conclusion, that the product of the action of formaldehyde on piperazine is dimethylene-dipiperazine (annexed formula). This would explain the action of hydrogen cyanide.

E. H.

**Quinazolines. XXI. Certain Quinazoline Oxygen Ethers of the Type  $\cdot N:C(OR)\cdot$  and the Isomeric  $\cdot NR\cdot CO\cdot$  Compounds.** MARSTON T. BOGERT and CLARENCE EARL MAY (*J. Amer. Chem. Soc.*, 1909, 31, 507—513).—In an earlier paper (Bogert and Seil, *Abstr.*, 1907, i, 560) an account was given of the formation and properties of two series of quinazoline derivatives, namely, the *O*-derivatives,  $\cdot C(OR):N\cdot$ , and *N*-derivatives,  $\cdot CO\cdot NR\cdot$ . In continuing the study of these compounds, *O*-ethers have been prepared by the action of alkyl oxides on the chloroquinazolines, and *N*-ethers by direct alkylation of the 4-quinazolones (4-hydroxyquinazolines) with alkyl halides, as well as by other methods described in previous papers. When 4-quinazolones are treated with alkyl iodides in presence of sodium ethoxide, a mixture of the *O*- and *N*-ethers is produced, but in the case of methyl, ethyl, *n*-propyl, and *n*-butyl iodides, the proportion of the *O*-ether formed is exceedingly small. The *N*-compounds are colourless, odourless solids, soluble in water, difficultly volatile with steam, of higher m. p. than the *O*-isomerides, and are not hydrolysed by strong hydrochloric acid. The *O*-compounds are oily liquids or solids of low m. p., usually of pleasant odour, readily volatile with steam, less soluble in water than the *N*-isomerides, and are readily hydrolysed by hydrochloric acid with formation of the corresponding hydroxy-quinazolines (quinazolones). The following compounds are described.

The mercuric chloride compound of 2-ethoxyquinoline melts at 136—138°. 2-isoAmyloxyquinoline,  $C_6H_4 \begin{smallmatrix} N=C\cdot OC_5H_{11} \\ | \\ CH:CH \end{smallmatrix}$ , is readily hydrolysed by hydrochloric acid with formation of carbostyryl.

1-isoAmyl-2-quinolone,  $C_6H_4 \begin{smallmatrix} N(C_5H_{11})\cdot CO \\ | \\ CH=CH \end{smallmatrix}$ , forms a mercuric chloride compound, m. p. 89—90° (uncorr.). 2-isoAmyloxyepidine,



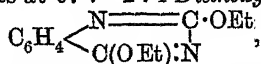
has m. p. 120—140°, and b. p. above 360°.

4-Methoxyquinazoline,  $C_6H_4 \begin{smallmatrix} N=CH \\ | \\ C(OMe):N \end{smallmatrix}$ , m. p. 35·4°, and 4-ethoxyquinazoline, m. p. 42—44°, form colourless crystals. 4-*n*-Propoxyquinazoline and 4-*n*-butoxyquinazoline are colourless oils, which boil at 257—260° and 263—265° respectively. 3-*n*-Propyl-4-quinazolone,  $C_6H_4 \begin{smallmatrix} N=CH \\ | \\ CO\cdot NPr^a \end{smallmatrix}$ , m. p. 82—83°, and the corresponding *n*-butyl compound, m. p. 73°, crystallise in needles.

When tetrachloro-2-methylquinazoline,  $C_6HCl_3 \begin{smallmatrix} N=CMe \\ | \\ CCl:N \end{smallmatrix}$  (Dehoff,

Abstr., 1891, 84), is treated with sodium methoxide, *trichloro-4-methoxy-2-methylquinazoline*,  $C_6HCl_3 \begin{smallmatrix} N=CMe \\ C(OMe):N \end{smallmatrix}$ , m. p. 87—88°, is obtained in colourless, silky needles. *Tetrachloro-2-ethylquinazoline*,  $C_6HCl_3 \begin{smallmatrix} N=C Et \\ CCl:N \end{smallmatrix}$ , m. p. 80°, obtained by heating 2-ethyl-4-quinazoline with phosphorus pentachloride and oxychloride, forms minute, colourless needles. Trichloro-4-ethoxy-2-methylquinazoline has the properties ascribed to it by Dehoff (*loc. cit.*).

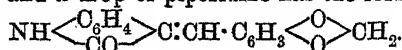
*2-Methoxyquinazoline*,  $C_6H_4 \begin{smallmatrix} N=C \cdot OMe \\ CH:N \end{smallmatrix}$ , m. p. 55—56°, crystallises in needles. *2-Ethoxyquinazoline* was obtained as a yellow oil, which, on cooling, forms cubical crystals. *2:4-Dimethoxyquinazoline* (Abt, Abstr., 1889, 610) melts at 67°. *2:4-Diethoxyquinazoline*,



m. p. 50—51°, forms silky needles. *2:4-Di-n-propoxyquinazoline*, m. p. 40—41°, crystallises in long needles. *1:3-Dimethylbenzoylenecarbamide* (Abt, *loc. cit.*) melts at 163—165°. *2:4-Diketo-1:3-diethylquinazoline*,  $C_6H_4 \begin{smallmatrix} NEt \cdot CO \\ CO \cdot NEt \end{smallmatrix}$ , m. p. 105—106°, forms minute, colourless needles. By the action of *n*-propyl iodide on benzoylenecarbamide in presence of alcoholic sodium hydroxide, *2:4-diketo-1-(or 3)-n-propylquinazoline*, m. p. 171°, is produced, but a dipropyl derivative could not be obtained.

E. G.

**A New Isomeride of Indigo.** ANDRÉ WAHL and P. BAYARD (*Compt. rend.*, 1909, 148, 716—719).—Oxindole condenses with aromatic aldehydes, giving coloured, crystalline compounds, which are isomeric with the indogenides (Baeyer, Abstr., 1884, 73). The compound obtained by boiling an alcoholic solution of oxindole with piperonaldehyde and a drop of piperidine has the formula



This crystallises in bright yellow, silky needles, m. p. 228—229°. The name *isoindogenides* is proposed for compounds of this type.

*3:3-Bisindole*,  $NH \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ C_6H_4 \\ \diagdown \quad \diagup \\ CO \end{smallmatrix} C:C \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ C_6H_4 \\ \diagdown \quad \diagup \\ CO \end{smallmatrix} NH$ , is prepared by heating on a water-bath oxindole and isatin in acetic acid containing a little hydrogen chloride.

The substance is sparingly soluble in ether, alcohol, and acetic acid, but crystallises from absolute methyl alcohol in garnet-red, acicular plates. When heated on platinum it melts above 350°, evolving yellow vapours. It is conveniently purified by sublimation in a vacuum.

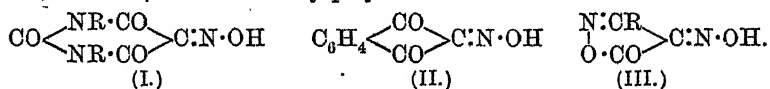
The existence of this new isomeride of indigotin affords conclusive proof of the correctness of the generally-accepted formula for indigored. The latter has been prepared by a new synthesis, which consists in condensing oxindole with isatin chloride under the same conditions as described in connexion with the preparation of the phenylisoxazolones (this vol., i, 261).

W. O. W.

**Pantochromism and Chromoisomerism of Violurates and Allied Oximinoketone Salts.** ARTHUR HANTZSCH (*Ber.*, 1909, 42, 966—985).—A theoretical paper, in which the results obtained by the author and his co-workers (see following abstracts) during their investigations on the colour of the salts of violuric acid and of closely-related compounds are discussed. An explanation of many of the facts observed cannot yet be given, and although investigations on this subject are still in progress, these results are now published owing to the appearance of a paper by Dimroth (this vol., i, 62).

It has already been shown that the production of coloured salts from colourless acids and colourless metals must be accompanied by a constitutional rearrangement, namely, an alteration of the manner in which the atoms are linked together; this change may occur without rearrangement of the atoms themselves within the molecule. Further, when a hydrogen compound in the solid state or in solution differs optically from its alkyl derivatives, it points to a constitutional change; for example, the esters of the so-called violuric acids having the formula  $\text{CO} \begin{smallmatrix} \text{NR} \cdot \text{CO} \\ \text{NR} \cdot \text{CO} \end{smallmatrix} \text{C} : \text{NOR}$  are esters of  $\psi$ -violuric acid (*leucoluric acid*), since they are quite colourless, and correspond, chemically, with the colourless salts, but not with the ordinary chromo-salts of these acids.

Many of the open-chain monoximes of diketones, particularly the colourless compounds, yield only colourless salts; apparently, polychromatic salts are only obtained from cyclic oximinoketones. Nevertheless, there are certain oximinoketones which yield salts with colourless metals having the same colour as the parent substance and its true oxime-ethers; thus, the ethers and salts of isatoxime have the same yellow colour as the parent substance. The salts of violuric acid, methylvioluric acid, dimethylvioluric acid, diphenylvioluric acid (I), oximinodiketohydrindene (II), and the oximino-oxazolones (III) are, however, extraordinarily polychromatic:



The preparation and analysis of several hundreds of salts of these compounds has led to the establishment of the following tenet: colourless or faintly-coloured cyclic oximinoketones yield salts with colourless metallic and ammonium ions which are red, orange, yellow, green, blue, violet, sometimes brown, olive-green, greenish-violet, flesh-coloured, and occasionally colourless. In other words, the

complex  $\text{X} \begin{smallmatrix} \text{C} \cdot \text{O} \\ \text{C} \cdot \text{N} \cdot \text{O} \end{smallmatrix} \} \text{M}_1, \text{M}_2, \dots, \text{M}_n$ , where X represents a cyclic nucleus and M a metal, is *pantochromatic*, depending on the nature of the colourless or faintly-coloured anion and the colourless cation. As a general rule, a salt of one colour only is obtained with each individual colourless metallic or ammonium ion; particularly is this true when the same method of preparation is employed. Sometimes, however, the colour of the salt as initially precipitated changes; this change of colour is effected more frequently by altering the tempera-

ture or the solvent. It is proposed to distinguish this variation of colour of one and the same salt by the word *chromotropy*, and to designate salts which exist in differently-coloured modifications as *variochromatic*. As examples of chromotropes of variochromatic salts may be cited the blue potassium, rubidium, and caesium violurates, which change into red salts without loss of weight when heated under moist benzene at 140–150°; the rubidium salt of oximino-*p*-bromophenyloxazolone is pink (labile), bluish-violet (labile), or violet (stable), whilst the corresponding caesium salt is pink (stable), bluish-violet (labile), or violet (labile). The stability of the different modifications of a variochromatic salt is extremely variable; generally, the velocity of transformation of the dry, solid salt is very small. Definite relationships between the nature of the colourless metal and the stability and colour of the salt have not yet been established. As a rule, the lithium salts are yellow, orange, or red; blue and violet salts have hitherto not been isolated; only the orange and red sodium salts are stable; occasionally labile blue and violet sodium salts are obtained; the stable potassium, rubidium, and caesium salts are usually blue, bluish-green, or violet, whilst the labile salts are red; orange salts of these metals have not been obtained.

In many cases, combination of the solvent with the salt alters the colour; thus, the silver salt of oximinomethyloxazolone is red; the compound with  $\frac{1}{2}\text{C}_5\text{NH}_5$  is pink, that with  $2\text{NH}_3$  is violet, and that with  $\text{C}_5\text{H}_{11}\text{N}$  is violet. The change of colour is not directly due to the combination of the salt with the solvent, since the potassium, rubidium, and caesium salts of oximino-*p*-bromophenyloxazolone with and without ethyl alcohol are pink, but is produced indirectly, in that the solvent renders stable an otherwise labile chromotrope. Sometimes the additive compounds themselves are variochromatic; thus, silver dimethylviolurate with  $\text{C}_5\text{NH}_5$  exists in a stable, bluish-violet form and a labile, green form.

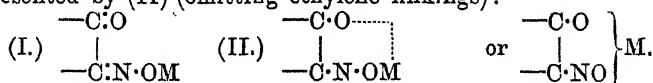
Solutions of the variochromatic modifications of one and the same salt in the same solvent are identical.

Strong solutions of the same salt in different solvents, however, have different colours. The colour of the solutions of the salts with various alkali-metals becomes deeper as the atomic weight of the metal increases; thus, in acetone, the solution of the lithium salt of oximino-*p*-bromophenyloxazolone is carmine, the sodium salt is violet, the potassium salt is violet-blue, the rubidium salt is bluish-violet, and the caesium salt is blue. The colour of the same salt in non-dissociating solvents is weakened by "negative" solvents (phenol, etc.) and strengthened by "positive" solvents (ammonia, amines, etc.); thus, the solutions of the potassium, rubidium, and caesium salts of oximino-*p*-bromophenyloxazolone in phenol are red, in acetone bluish-violet, and in pyridine, blue.

Mol.-wt. determinations show that the polychromatic salts are unimolecular, consequently the various polychromatic salts are constitutively different, and the variochromatic salts are true isomeric salts. All attempts to obtain isomeric alkyl and acyl derivatives from the variously-coloured salts have been unsuccessful; in some cases, however, differences in the reaction-velocities were observed;

for example, the blue silver salt of oximino-*p*-bromophenyloxazolone explodes when treated with methyl iodide, whilst the red silver salt when similarly treated merely reacts with a great development of heat.

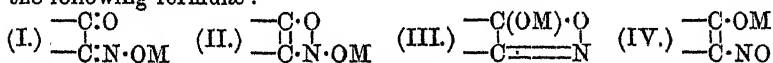
Since salts of simple oximes,  $>\text{C}:\text{N}\cdot\text{OM}$ , are colourless, whereas the oximinoketone salts are coloured, it follows that the production of colour is due to the presence of the carbonyl group; consequently, if the *leuco*-salts have the formula (I), the *chromo*-salts may be represented by (II) (omitting ethylene linkings):



It is possible to account for the production of colour in this way, but not the occurrence of pantochromatic salts. The possibility that pantochromism may be produced by the various metals occupying different positions relative to the carbonyl oxygen atom and the oxime oxygen atom, such positions depending on the different affinities of the various metals for one or other oxygen atom, is considered improbable.

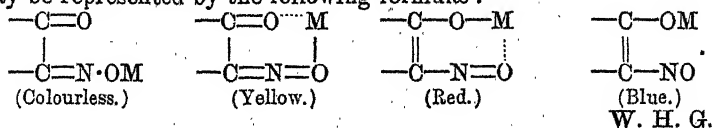
Notwithstanding the extraordinary diversity of colour of the salts of the violuric acids, it is found that about one-half are carmine, whilst the members of a smaller group comprising the potassium, rubidium, caesium, and ammonium salts are bluish-violet to blue, and those of a third group of about equal numbers containing several lithium salts and the acid salts of dimethylvioluric acid are yellow. The same applies to the salts of the oximino-oxazolones; in fact, the primary colours of the salts of oximinoketones are yellow, red, and blue; the other coloured salts are mixed salts, for example, the violet salts are mixtures of blue with red salts.

The existence of the colourless, yellow, red, and blue isomerides may be explained by assuming that they are structural isomerides having the following formulæ:



Since the *chromo*-salts are so similar in their chemical behaviour, it is very improbable, however, that they are structural isomerides.

A third explanation, depending on the presence and varied distribution of the partial valencies of the atoms of the unsaturated chromophoric complex and the partial valencies of the metallic atoms, may also be given. The four primary forms of the salts of oximinoketones may be represented by the following formulæ:



**Salts and Esters of the Violuric Acid Group.** ARTHUR HANTZSCH and P. C. C. ISHERWOOD (*Ber.*, 1909, 42, 986—1000. Compare preceding abstract; Wagner, *Abstr.*, 1894, ii, 8; Guinchard, *Abstr.*, 1899, i, 779).—A large number of salts of colourless metals

with violuric acid, methylvioluric acid, and dimethylvioluric acid have been prepared, and the majority analysed. Contrary to the statement of Andreasch (Abstr., 1895, i, 336), acid salts are also formed; the first two acids also yield dimetallic derivatives. The colourless methyl and benzyl esters of the three acids have also been prepared. The esters of violuric acid yield colourless mono- and di-metallic salts; the esters of methylvioluric acid yield colourless mono-metallic salts. Since these esters and salts are colourless, they must be regarded as derivatives of  $\psi$ -violuric acid or *leucoluric acid*.

About 100 violurates have been prepared, of which 73 are red, 10 bluish-violet, 10 yellow, 5 green, and the others colourless; 22 of the 31 dimetallic salts are red.

*Benzyl violurate*,  $C_4H_2O_2N_3 \cdot C_7H_7$ , prepared by the action of  $\alpha$ -benzylhydroxylamine on alloxan, crystallises in colourless leaflets, decomposing at  $222^\circ$ ; the *sodium*, *potassium*, *ammonium*, *silver*, *disodium*, and *dipotassium* salts are colourless; the *disilver* salt is slightly yellow.

*Benzyl dimethylviolurate*,  $C_{13}H_{13}O_4N_3$ , has m. p.  $164^\circ$ .

*Salts of Violuric Acid*.—The *lithium* salt,  $C_4H_2O_2N_3Li$ , is a carmine-red powder; the *sodium* salt forms red needles; the *potassium* salt ( $2H_2O$ ) crystallises in bluish-violet needles; the *rubidium* salt from water is bluish-violet, and from alcohol is pure blue; the *cesium* salt is blue; the *ammonium* salt from water is bluish-violet, and from alcohol is pure blue; the *glucinium* salt crystallises in dark red prisms; the *magnesium*, *calcium*, *strontium*, and *barium* salts form red needles; the *zinc* salt ( $2H_2O$ ) forms reddish-brown needles; the *anhydrous* salt is carmine; the *cadmium* salt is brownish-red; the *thallium* salt forms red leaflets; the *lead* salt crystallises in dark red needles; the *silver* salt is practically colourless when first precipitated at  $-15^\circ$ , and becomes grey, violet, or green when dry; it passes into small, heavy, dark green crystals when kept for some time under the liquid; the *dilithium* salt,  $C_4H_2O_4N_3Li_2$ , is pure yellow; the *disodium*, *dipotassium*, *dirubidium*, and *dicaesium* salts are dark red; the *diammonium* salt is light red; the *dibarium*, *distrontium*, *dimagnesium*, and *dilead* salts are red powders; the *disilver* salt is dark green; the *hydrogen potassium*, *hydrogen rubidium*, and *hydrogen caesium* salts are obtained as dark red crystals; the *hydrogen thallium* salt forms pale green leaflets; the *hydrogen silver* salt,  $(C_4H_2O_4N_3)_2Hg \cdot 3H_2O$ , crystallises in red, hexagonal plates.

*Salts of Dimethylvioluric Acid*.—The *lithium* salt,  $C_6H_6O_4N_3Li$ , crystallises in pale carmine needles; the *sodium* salt is also pale carmine; the *rubidium* and *caesium* salts are bluish-violet; the *glucinium* salt forms brownish-red plates; the *thallium* salt is dark red; the *silver* salt is reddish-brown; the blue silver salt described by Andreasch (*loc. cit.*) is a *potassium silver* salt,  $(C_6H_6O_4N_3)_2KAg$ ; the *hydrogen rubidium*, *hydrogen caesium*, *hydrogen ammonium*, and *hydrogen thallium* salts are orange-yellow; the *hydrogen silver* salt forms red, transparent needles.

*Chromotropy of Solid Violurates*.—The *blue* potassium, rubidium, and caesium violurates when heated with moist benzene under pressure at  $140^\circ$  pass into *red* modifications; the *red* sodium salt when

similarly treated becomes slightly lighter; the *carmine* lithium salt when heated with moist benzene at  $170^{\circ}$  passes into a *brownish-yellow* modification; the *bluish-violet* potassium methylviolurate when treated in the same manner yields a *dark red* variety. The dimethylviolurates do not change colour when similarly treated.

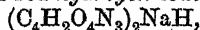
W. H. G.

**Polychromatic and Chromotropic Violurates.** ARTHUR HANTZSCH and BASILE ISSAIAS (*Ber.*, 1909, 42, 1000—1007. Compare preceding abstract).—An investigation on the formation and properties of several chromotropes of violurates and dimethylviolurates. It is found that the salts of these acids with the alkali metals exist in at least three differently coloured forms: yellow, red, and blue, or the corresponding mixed colours. Each alkali salt can exist in at least two modifications, either yellow and red or red and blue, one of which is always stable; thus, the red salts of lithium and sodium, and the blue salts of potassium, rubidium, and caesium, are stable; yellow salts are obtained only with lithium and are labile.

Silver violurates in combination with colourless components, such as pyridine, silver nitrate, and alkali violurates, exist in colourless, yellow, red, blue, and green forms.

The labile violurates described below are obtained usually by one of the following methods: (1) heating the stable variety with moist benzene under pressure at  $140$ — $150^{\circ}$ ; (2) heating the stable variety with water vapour at a temperature slightly above  $100^{\circ}$ ; (3) precipitation from alcoholic solution with ether; (4) preparation of the salt in absolute alcoholic solution. In some cases, the formation of the labile modification is dependent on the presence of catalysts, the nature of which is sometimes unknown.

Potassium violurate may be obtained as small *red* crystals, and also as a *pale pink* precipitate by precipitation in absolute alcohol at  $-70^{\circ}$ . The red sodium salt becomes *bluish-violet* at  $150^{\circ}$ . A *yellow* lithium salt is obtained by evaporating a methyl-alcoholic solution in a desiccator. *Silver dipyridine violurate*,  $C_4H_2O_4N_3Ag \cdot 2C_5H_5N$ , is obtained as microscopic, colourless needles by adding ether to a solution of silver violurate in pyridine; it becomes blue when kept. A stable red *sodium silver violurate* is prepared by treating a solution of sodium violurate with silver nitrate. A stable blue *potassium silver violurate* is obtained by similar means; a labile red potassium silver salt is formed by treating dipotassium violurate with strong aqueous silver nitrate. A red *hydrogen sodium violurate*,



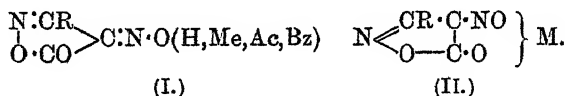
and orange-yellow *hydrogen potassium* salt have also been prepared.

Various coloured dimetallic salts have also been prepared, for example, a yellow *lithium silver* salt. The labile lithium dimethylviolurate crystallises in *yellow* needles; the ordinary red sodium salt ( $3H_2O$ ), when heated at  $150^{\circ}$ , becomes *violet*, and then contains about 1% of water; it becomes again red at the ordinary temperature; a stable *blue* potassium dimethylviolurate may be obtained by boiling the violet salt ( $\frac{1}{2}H_2O$ ) with methyl alcohol; the violet salt becomes *red* at about  $-70^{\circ}$ .

W. H. G.

**Polychromatic Salts from Oximino-oxazolones.** ARTHUR HANTZSCH and W. KEMMERICH (*Ber.*, 1909, 42, 1007—1015. Compare preceding abstracts).—The salts of the colourless or faintly

yellow oximino-oxazolones,  $\begin{matrix} \text{N:CR} \\ | \\ \text{O} \cdot \text{CO} \end{matrix} > \text{C:N} \cdot \text{OH}$ , with colourless metals, like the violurates, exist in yellow, red, and blue modifications; occasionally, orange, violet, and green salts are obtained. From this it follows that pantochromism is not dependent on the presence of the complex  $\cdot \text{CO} \cdot \text{C}(\text{NOH}) \cdot \text{CO} \cdot$ , and that two, and only two, negative, unsaturated groups are necessary for the production of the chromophore in the salt formation. The alkyl and acyl derivatives, unlike the polychromatic salts, are colourless or but faintly yellow, consequently they must have the formula I, whilst the salts have the general formula II.



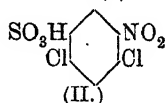
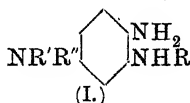
**Derivatives of Oximinophenyloxazolone.**—The salts of oximinophenyl-oxazolone are stable in the dry state and in indifferent solvents; they explode when heated, even below 100°. The *lithium* and *sodium* salts are vermilion; the *potassium* salt,  $\text{C}_9\text{H}_5\text{O}_3\text{N}_2\text{K}$ , crystallises in small, violet needles, which become blue when kept; the *hydrate* ( $1\text{H}_2\text{O}$ ) forms red needles; the violet *rubidium* salt also becomes blue when kept; the *caesium* salt is bluish-violet and deliquescent; the *ammonium* salt forms garnet-red needles; the *tetramethylammonium* salt is deep blue; the *barium* salt is pink; the *calcium* salt is orange-red; the *acid potassium*, *rubidium*, and *caesium* salts are yellow; the *hydrogen sodium* salt is pink; an apparently colourless *silver* salt is obtained by precipitating the ammonium salt in alcoholic solution with silver nitrate at  $-30^\circ$ ; by varying the method of preparation, a pink, vermilion, carmine, or blue silver salt may be obtained; the *hydrogen silver* salt,  $(\text{C}_9\text{H}_5\text{O}_3\text{N}_2)_2\text{HAg}$ , exists in a yellow and orange form; the *potassium silver* salt,  $(\text{C}_9\text{H}_5\text{O}_3\text{N}_2)_2\text{AgK}$ , is blue; the salt,  $\text{C}_9\text{H}_5\text{O}_3\text{N}_2\text{Ag} \cdot \text{AgNO}_3$ , is olive-green; the *silver dipyridine* salt,

$\text{C}_9\text{H}_5\text{O}_3\text{N}_2\text{Ag} \cdot 2\text{C}_5\text{H}_5\text{N}$ , forms violet crystals; the *silver diammonia* salt,  $\text{C}_9\text{H}_5\text{O}_3\text{N}_2\text{Ag} \cdot 2\text{NH}_3$ , is blue; the *thallium* salt is red; the *pyridine* salt is brick-red; the *piperidine* salt is scarlet; the *ethyl* ester,  $\text{C}_{11}\text{H}_{10}\text{O}_3\text{N}_2$ , is pale yellow, and has m. p.  $113^\circ$  (decomp.); the *acetate*,  $\text{C}_{11}\text{H}_8\text{O}_4\text{N}_2$ , is slightly yellow, and has m. p.  $155^\circ$ ; the *benzoate*,  $\text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_2$ , is quite colourless.

**Salts of Oximinomethyloxazolone.**—The *sodium* salt is light red; the *potassium* salt is violet; the *potassium hydrogen* salt is yellow; the *barium* salt is pink; the *silver pyridine* salt,  $\text{C}_4\text{H}_5\text{O}_3\text{N}_2\text{Ag} \cdot \frac{1}{2}\text{C}_5\text{H}_5\text{N}$ , is pink; the *silver ammonia* salt,  $\text{C}_4\text{H}_5\text{O}_3\text{N}_2\text{Ag} \cdot 2\text{NH}_3$ , is reddish-violet; the *piperidine* salt is orange; the *pyridine* salt is lemon-yellow.

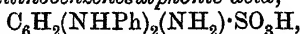
W. H. G.

[Preparation of Derivatives of Triaminobenzene.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 205358).—Derivatives of 1:2:4-triaminobenzene, having the general formula (I), are readily



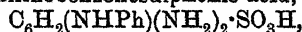
obtained from 2:4-dichloro-5-nitrobenzenesulphonic acid by successively condensing with organic bases and reducing the nitro-group.

5-Amino-2:4-dianilinobenzenesulphonic acid,



a colourless, sparingly soluble powder, is thus obtained by heating 2:4-dichloro-5-nitrobenzenesulphonic acid (II) with aqueous aniline at 120—150° in the presence of some substance, such as chalk, sodium carbonate, or sodium acetate, for neutralising the hydrogen chloride liberated. The intermediate nitrodianilinobenzenesulphonic acid is then reduced with iron and acetic acid, or with alkaline sodium hyposulphite.

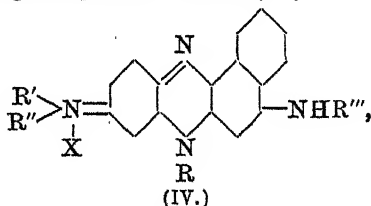
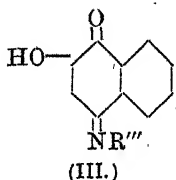
2:5-Diamino-4-anilinobenzenesulphonic acid,



colourless, lustrous, sparingly soluble leaflets, was obtained by the following series of operations.

Sodium 2-chloro-5-nitro-4-anilinobenzenesulphonate, yellow crystals, soluble in hot water, was produced by heating together 2:4-dichloro-5-nitrobenzenesulphonic acid (1 mol.), aniline (1 mol.), and aqueous sodium acetate. This product, on heating with 20% ammonium hydroxide at 150°, gives sodium 5-nitro-2-amino-4-anilinobenzenesulphonate, lustrous, yellow leaflets, which on reduction yields the foregoing diamine.

These triaminobenzene derivatives when condensed with the  $\beta$ -hydroxynaphthaquinoneimides (III), or their sulphonic acids, give rise to naphthasafranines having the general formula (IV):



where R is an alkyl or aryl group, and R', R'', and R''' are hydrogen, alkyl, or aryl radicles.

These dyes furnish red to greenish-blue shades, suitable either for wool or silk.

F. M. G. M.

Derivatives of Osotetrazines and Osotriazoles. ROBERT STOLLÉ (*Ber.*, 1909, 42, 1047. Compare Pechmann and Bauer, this vol., i, 270; Stollé, this vol., i, 123).—Polemical. Stollé was the first to

ascribe to diphenylosotetrazine the constitution of a 1-amino-3:4-diphenyl-1:2:5-triazole.  
E. F. A.

**Behaviour of a Diazo-salt towards Organic Solvents.** GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1909, 44, 232—243).—Under the influence of various organic solvents, the *p*-bromodiazobenzene derivative of *o*-dinitrotoluene,  $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Br}$ , undergoes two distinct intramolecular transformations, yielding: (1)  $\alpha$ -nitro- $\beta$ -nitroso- $\alpha$ -benzoyl- $\beta$ -*p*-bromophenylhydrazine, which may then, by losing two atoms of nitrogen and three of oxygen in the form of nitrous compounds, become converted into benzoylazo-*p*-bromobenzene, and (2)  $\omega$ -*p*-bromobenzeneazo-*o*-dinitrotoluene.

The *p*-bromodiazobenzene salt of *o*-dinitrotoluene,  
 $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Br}$ ,  
prepared by the action of *p*-bromodiazobenzene acetate on the potassium derivative of *o*-dinitrotoluene, separates as a golden-yellow powder, m. p. 98° (decomp.).

$\alpha$ -Nitro- $\beta$ -nitroso- $\alpha$ -benzoyl- $\beta$ -*p*-bromophenylhydrazine,  
 $\text{NO}_2 \cdot \text{NBz} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NO}$ ,  
obtained by maintaining an anhydrous benzene solution of the above salt at 0°, separates in pale straw-yellow laminae, m. p. 121—122° (decomp.), gives Liebermann's reaction, and decomposes in moist air with evolution of nitrous vapours. Towards water, it behaves like other nitronitrosohydrazines previously described (compare Abstr., 1908, i, 482; Ponzio and Charrier, Abstr., 1908, i, 582), the nitro-group being readily replaced by an atom of hydrogen, yielding  $\beta$ -nitroso- $\alpha$ -benzoyl- $\beta$ -*p*-bromophenylhydrazine,  $\text{NHBz} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NO}$ , which separates in pale straw-yellow laminae, m. p. 123° (decomp.), gives Liebermann's reaction, and dissolves in concentrated sulphuric acid, yielding a wine-red solution; with alkalis, this compound forms salts, such as

$\text{NNaBz} \cdot \text{N}(\text{C}_6\text{H}_4\text{Br}) \cdot \text{NO}$ ,  
soluble in water to reddish-yellow solutions, whilst with hot water it behaves like other nitrosohydrazines (*loc. cit.*), losing the nitroso-group for a hydrogen atom and yielding  $\alpha$ -benzoyl- $\beta$ -*p*-bromophenylhydrazine. The latter compound can be readily converted back into its nitroso-derivative by the action of nitrous acid.

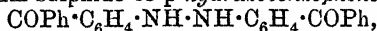
The transformation of the *p*-bromodiazobenzene salt of *o*-dinitrotoluene into benzoylazo-*p*-bromobenzene, m. p. 71° (Freer, Abstr., 1899, i, 357, gave 69°), takes place readily in presence of an organic solvent, such as benzene, ether, carbon disulphide, or chloroform, containing a small proportion of water.

$\omega$ -*p*-Bromobenzeneazo-*o*-dinitrotoluene,  $\text{CPh}(\text{NO}_2)_2 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$ , obtained in small proportion by the action of cold absolute alcohol on the *p*-bromodiazobenzene salt of *o*-dinitrotoluene, or by leaving the latter in a desiccator for eight to ten days, crystallises from chloroform in orange-red laminae, m. p. 162—163° (decomp.).

All the results obtained confirm the structure of  $\alpha$ -nitro- $\beta$ -nitroso- $\alpha$ -benzoyl- $\beta$ -*p*-bromophenylhydrazine, and also support the constitution,  $\text{NO}_2 \cdot \text{CPh}(\text{NO}) \cdot \text{O} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$ , for the compound obtained by the action of *p*-bromodiazobenzene acetate on the potassium derivative of *o*-dinitrotoluene.

T. H. P.

**Alkaline Reduction of the Three Nitrobenzophenones.** PAUL CARRÉ (*Bull. Soc. chim.*, 1909, [iv], 5, 277—283. Compare Abstr., 1907, i, 142).—When a boiling alcoholic solution of *o*-nitrobenzophenone is rapidly reduced by sodium hydroxide and zinc dust, the main product is *o*-aminobenzophenone; a small quantity of an inseparable mixture of *o*-hydrazodiphenylmethane and diphenylmethane-*o*-hydrazobenzhydrolis also obtained, which by treatment with concentrated hydrochloric acid yields from the former substance, 4:4'-diamino-3:3'-dibenzylidiphenyl, and from the latter, benzaldehyde and 4:4'-diamino-3-benzylidiphenyl,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CH}_2\text{Ph}$ , m. p. 209°, the salts of which are extensively dissociated in water. The reduction of *p*-nitrobenzophenone in a similar manner yields a mixture of *p*-azobenzophenone and *p*-azoxybenzophenone, which is reduced by boiling alcoholic ammonium sulphide to *p*-hydrazobenzophenone,

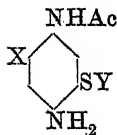


which separates from alcohol in white needles containing 1 mol.  $\text{H}_2\text{O}$ , m. p. 130° (162° when anhydrous); in boiling alcoholic solution the hydrazo-compound is oxidised by mercuric oxide to *p*-azobenzophenone, m. p. 219°, which separates from toluene in red leaflets and yields a *phenylhydrazone*,  $\text{C}_{38}\text{H}_{30}\text{N}_6$ , m. p. 130°.

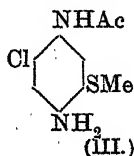
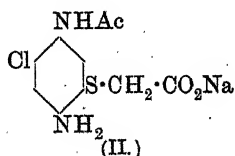
*m*-Nitrobenzophenone, reduced in a similar manner, yields Elbs and Wogrintz's *m*-azoxybenzophenone. C. S.

**Preparation of *O*-Acetyl Derivatives of the Aminophenols and Aminonaphthols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206455).—Excepting when the two substituents are in contiguous ortho-positions, the diazophenols and diazonaphthols can be readily acetylated with acetic anhydride in aqueous solutions containing only organic acids. The *O*-acetyl derivatives thus produced, although not isolated from solution, couple more readily with  $\beta$ -naphthol than the diazophenols themselves, giving azo-derivatives having distinctive colours. Solutions of 4-diazophenol and 8-diazo- $\alpha$ -naphthol-3:6-disulphonic acid were thus acetylated and the products coupled with alkaline  $\beta$ -naphthol. F. M. G. M.

[Preparation of Alkylthiol Derivatives of Primary Aromatic Amines.] KALLE & Co. (D.R.-P. 205421).—Amines having the general formula (I), when diazotised and combined with heteronuclear  $\alpha$ -naphthylaminesulphonic acids (such as the 1:6-sulphonic acid) and then hydrolysed to remove the acyl group, give rise to substantive bisazo-dyes, which when again diazotised on the cotton fibre can be coupled with  $\beta$ -naphthol to produce indigo shades of great fastness. In the foregoing formula, Y may be an alkyl, acyl,



(I.)



or  $\text{CH}_2 \cdot \text{CO}_2\text{H}$  radicle, whilst X may be alkyl, alkyloxy, or halogen. Dyes from the bases (II) and (III) are described in the patent. F. M. G. M.

**Hydrolysis of Egg-albumin by Sodium Hydroxide.** ZDENKO H. SKRAUP and F. HUMMELBURGER (*Monatsh.*, 1909, 30, 125—145).—An investigation on protalbic acid and lysalbic acid (compare Paal, *Abstr.*, 1902, i, 653). It is found that lysalbic acid is not a simple substance, but consists of a substance precipitated by ammonium sulphate, which it is proposed to name *egg-lysalbic acid*, and another substance, not precipitated by this reagent, which is designated *lysalbin-peptone*. Protalbic acid, when treated with sodium hydroxide, yields egg-lysalbic acid and lysalbin-peptone, whilst egg-lysalbic acid under similar conditions yields ammonia, hydrogen sulphide, and a small quantity of a substance soluble with difficulty in water. It is shown, however, that when egg-albumin is hydrolysed by sodium hydroxide, one part of the molecule yields protalbic acid, whilst the other part gives rise to egg-lysalbic acid and lysalbin-peptone. In order to obtain further information on the relationship existing between protalbic acid, egg-lysalbic acid, lysalbin-peptone, and egg-albumin, the hydrolysis of these substances by sulphuric acid was investigated quantitatively. The following table gives the results obtained, in parts %:

	Egg- albumin.	Protalbic acid.	Egg- lysalbic acid.	Lysalbin- peptone.
Histidine .....	1.5	2.3	0.3	0.6
Arginine .....	2.9	0.4	0.2	0.3
Lysine .....	3.9	3.3	5.3	4.0
Tyrosine .....	2.4	3.4	2.6	1.1
Phenylalanine .....	5.8	12.0	5.2	2.4
Proline .....	1.5	2.0	1.0	0.3
Amino-acids .....	7.9	14.7	7.0	3.2
Glutamic acids .....	3.2	1.8	1.0	1.6

Egg-lysalbic acid and lysalbin-peptone give with  $\alpha$ -naphthol and thymol the reactions which are characteristic of carbohydrate residues, whilst protalbic acid does not give these reactions.

It is therefore evident that the more stable part of the egg-albumin molecule which passes into protalbic acid consists chiefly of the aromatic components, whilst the so-called carbohydrate residue is present in the other part of the molecule, which breaks down into the albumose and peptone.

W. H. G.

**The Serum Proteins of Different Animals.** EMIL ABDERHALDEN and SLAVU (*Zeitsch. physiol. Chem.*, 1909, 59, 247—248).—Serum-albumin and serum-globulin were prepared by the ammonium sulphate method from goose's blood. Their yield of certain amino-acids was then determined, and the results compared with those from horse's blood may be given as follows in parts %.

		Tyrosine.	Glutamic acid.	Glycine.
Serum-albumin .....	horse	2.1	7.7	0.0
" .....	goose	1.25	8.1	0.0
Serum-globulin .....	horse	2.5	8.5	3.5
" .....	goose	2.45	9.1	3.62

W. D. H.

**Hydrolysis of Vitellin from the Hen's Egg.** THOMAS B. OSBORNE and D. BREESE JONES (*Amer. J. Physiol.*, 1909, 24, 153—160).—The amounts of amino-acids obtained are very similar to those previously given by Abderhalden and Hunter; glycine, however, was not found.

W. D. H.

**Some Picryl Derivatives of Protein Fission Products.** K. HIRAYAMA (*Zeitsch. physiol. Chem.*, 1909, 59, 290—292).—Picryl chloride, dissolved in toluene, is shaken with one equivalent proportion of the amino-acid dissolved in an equivalent of alkali hydroxide. The picryl derivatives of glycine,  $C_8H_5O_8N_4$ , m. p.  $161^\circ$ , valine,  $C_{11}H_{12}O_8N_4$ , m. p.  $171^\circ$ , and of aspartic acid,  $C_{10}H_8O_{10}N_4$ , m. p.  $137^\circ$ , are well crystallised and very sparingly soluble in cold water. Dipicryl-arginine and dipicrylhistidine were also prepared, but are not so readily obtained pure.

G. B.

**Electrolytes and Colloids. The Physical State of Gluten.** THOMAS B. WOOD and WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1909, B, 81, 38—43).—Gliadin (from wheat) is not soluble in distilled water or in acids of more than a certain critical concentration. Dilute acids, however, destroy the cohesion and form a hydrosol. Salt solutions in the presence of acids restore the cohesion. The effect of alkalis is similar to that of acids. The phenomena are in agreement with the hypothesis that the gluten hydrosol is a pseudo-solution in virtue of the existence of an electrical double layer round the gluten particles; this hypothesis receives support from the measurement of the potential difference between the two faces of the double layer by means of the electrical conductivity of the solutions of gluten in acids, and the rate of transport of the particles in a uniform electric field.

G. B.

**Action of Sulphur Dioxide on Flour and Cereals.** M. CARTERET and GEORGES CARTERET (*Bull. Soc. chim.*, 1909, [iv], 5, 270—272).—Flour or grain submitted to the action of sulphur dioxide for six hours suffers serious deterioration. The grain loses its germinating power, and both grain and flour, in consequence of some action of the sulphur dioxide on the gluten, yield a dough which can be kneaded only with difficulty and does not ferment with yeast; bread made from it is heavy and unfit for consumption.

C. S.

**Bleaching of Flour.** E. F. LADD and H. P. BASSETT (*J. Biol. Chem.*, 1909, 6, 75—86).—The modern process of bleaching or ageing flour by means of nitrogen peroxide is regarded as injurious. The bleached flour and the bread made from it are less susceptible to the action of digestive and other enzymes. It is suggested that the action on the gluten is a diazo-reaction, for nitrogen is evolved when the flour is treated with an acid. In extreme cases, the xanthoproteic reaction may be produced. The iodine absorption of the oil separated from patent flour is lessened by bleaching; the oil also contains nitrogen.

W. D. H.

**Oxyhæmoglobin of Different Animals. I.** EMIL ABDERHALDEN and FLORENTIN MEDIGRECEANU (*Zeitsch. physiol. Chem.*, 1909, 59, 165—169).—The oxyhæmoglobin of mammals yields a high percentage of histidine; the relationship of this substance to the purine group suggests that in non-nucleated corpuscles it may play the part of a nuclear material; but this hypothesis was negatived by the finding that the hæmoglobin from the nucleated corpuscles of birds contains also a high percentage of the same base. The hæmoglobin of birds' corpuscles was prepared in crystalline form, and the purer the crystals the less phosphorus do they contain, which confirms the view so generally held, that phosphorus is due to admixture with nuclein.

W. D. H.

**A New Hæmatin.** FRANCESCO DE GRAZIA (*Biochem. Zeitsch.*, 1909, 16, 277—293).—In gastric digestion of blood in the presence of mineral or organic acids, or a mixture of both, a hæmatin is formed which resembles acid-hæmatin spectroscopically, but contains less nitrogen. The formula given is  $C_{33}H_{35}O_7N_2Fe_4$ .

W. D. H.

**Synthesis of Paranuclein through the Agency of Pepsin and the Chemical Mechanics of the Hydrolysis and Synthesis of Proteins through the Agency of Enzymes.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1909, 5, 493—523. Compare Armstrong, Abstr., 1906, i, 217; Neuberg, 1907, i, 808).—The synthesis of protein as effected by large quantities of trypsin or pepsin is not in agreement with the hypothetical reaction of pure catalysts in accelerating both forward and reverse reactions. Experiments with paranuclein and pepsin indicate that the velocity constant of hydrolysis diminishes with increasing substrate concentration; the velocity of synthesis falls off abruptly when the pepsin concentration falls below a certain value. Excess of pepsin shifts the equilibrium between paranuclein and its products. Synthesis occurs at a temperature  $10^\circ$  to  $15^\circ$  above the "death-point" of pepsin; the conclusion is drawn that the synthetic agent is not identical with the hydrolytic enzyme.

The relation between protein and enzyme is assumed to be reciprocal. The enzyme carries water into the protein molecule and, parting with it, recoups itself from the medium, while the protein splits up into the products of hydrolysis. The products of protein hydrolysis are assumed to part with water to the anhydrous form of the enzyme, whereby protein is regenerated and the hydrated form of the enzyme set free. A definite ratio between the velocities of these two reciprocal processes exists; this determines the final equilibrium of the system both as regards the relative proportions of protein and the products of its hydrolysis, and also the relative proportions of anhydrous (synthetic) and hydrated (hydrolytic) enzyme.

The relation between the anhydrous and hydrated forms of the enzyme may be similar to that between the internal salt and the hydrated forms of an amino-acid.

E. F. A.

**Reducing Component of Nucleic Acid from Yeast.** WILLIAM F. BOOS (*J. Biol. Chem.*, 1909, 5, 469—476).—The reducing substance obtained from yeast nucleic acid cannot be a pentose. Its simplest empirical formula is  $C_7H_8O$ . It is not yet identified.

W. D. H.

**Alteration of Gelatin Solutions. Determination of their Gold Numbers and Ultra-microscopic Observations.** W. MENZ (*Zeitsch. physikal. Chem.*, 1909, 66, 129—137).—In order to test the widely held view, recently disputed by Pauli, that the gelatinisation of gelatin solutions on cooling is attended by the separation of a new phase, the author has examined gelatin solutions of varying concentrations with the ultra-microscope and has determined their gold number according to Zsigmondy; the results show that not only the solidified mixtures, but even fairly weak solutions of gelatin, are heterogeneous.

According to Zsigmondy, the gold number of a protective colloid is the number of mgs. which is just insufficient to prevent a definite change of colour (in the present case from red to purple) in a dilute solution of colloidal gold on the addition of 1 c.c. of a 10% solution of sodium chloride. The preparation of a gold solution suitable for the experiments is fully described. It has been found that the gold numbers of solutions one day old of concentrations from 0.001% to 1% are the greater the more concentrated the solution. The numbers in the case of the concentrated solutions remain fairly constant on keeping, but those of the weakest solutions increase rapidly at first and then become constant. In the ultra-microscope, the solutions from 0.1% to 1% show a heterogeneous cone of light; the less concentrated solutions (from 0.01%) also show a light cone, which, however, is no longer resolvable, and in the weakest solution (0.001%) is only just noticeable.

From these observations the conclusions are drawn (1) that the protective action of the gelatin is due to the amicroscopic particles, or, perhaps, to the smallest particles visible in the ultra-microscope; the larger particles have little or no protective action; (2) the state of the gelatin in aqueous solution depends essentially on its concentration after the latest warming; it is not greatly altered by dilution with cold water.

Some experiments on the precipitation of colloidal gold by gelatin alone are described. Further, the phenomena observed when a gelatin solution solidifies under the ultra-microscope are described and figured.

G. S.

**Comparative Investigation of the Composition and Structure of Various Kinds of Silk. II. The Mono-amino-acids of Canton Silk.** EMIL ABDERHALDEN and LOTTE BEHREND (*Zeitsch. physiol. Chem.*, 1909, 59, 236—238).—The results are in close agreement with those obtained by Fischer and Skita for (Italian) silk-fibroin (*Abstr.*, 1901, i, 783). In the hydrolysis only traces of melanins remained undissolved. The phenylalanine is best purified as hydrochloride.

G. B.

**Physical Constants of Peptones.** L. LEMATTE and A. SAYÈS (*Compt. rend.*, 1909, 148, 553—554).—The densities, refractive indices, and freezing points of aqueous solutions of trypsin peptones have been determined. Analysis of the peptones gave 16.8% nitrogen and 0.756% chlorine. If  $P$  is the number of grams of peptone contained in 100 c.c. of solution, the density at  $15^{\circ}$  is given by  $D = 1 + P \times 0.003637$ ; the difference between the refractive index and that of water at  $17.5^{\circ}$  by  $n = P \times 0.001869$ , and the lowering of the freezing point by  $\Delta = P \times 0.119$ .  
H. M. D.

**Clupeone.** ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1909, 59, 281—284. Compare Abstr., 1907, i, 266).—This protone, obtained by boiling clupeine for three hours with 10% sulphuric acid, yields a crystalline picrolonate. After removal of the picrolonic acid, the regenerated base contains the same percentage of arginine-nitrogen, namely, 88%, as that found by Pringle in clupeone.  
G. B.

**Action of Some Acid Chlorides on Protamines.** K. HIRAYAMA (*Zeitsch. physiol. Chem.*, 1909, 59, 285—289).— $\beta$ -Naphthalenesulphonylclupeine and benzenesulphonylclupeine have respectively about half and the whole of the basic hydrogen replaced; both are amorphous.  $\beta$ -Naphthalenesulphonylclupeone, prepared from the crystalline picrolonate (compare preceding abstract), is crystalline, and has a composition corresponding with that of a diarginylmonoamino-acid, as supposed by Kossel and Pringle (Abstr., 1907, i, 226); thus the sulphur and nitrogen content agree with that of a tetranaphthalenesulphonyl derivative of diarginylvaline,  $C_{57}H_{68}O_{28}N_9S_4$ . The benzenesulphonyl and  $\beta$ -naphthalenesulphonyl derivatives of sturine are amorphous.  
G. B.

**Composition and Derivation of Protamine.** ALONZO E. TAYLOR (*J. Biol. Chem.*, 1909, 5, 389—398).—Salmine (the protamine of the salmon) yields on hydrolysis arginine, an aminovaleric acid, serine, and proline (Kossel and Dakin); Abderhalden adds leucine, alanine, and probably phenylalanine and aspartic acid to the list. With purified salmine, Abderhalden's results are not confirmed; he was possibly dealing with an impure product, such as is obtained from the unripe roe. A theory that the protamine is derived from the muscle-proteins is put forward; these are believed to be converted into the blood-proteins for transport, and these into protamines by the testis through the intermediate stage of histone.  
W. D. H.

**Synthesis of Protamine through Ferment Action.** ALONZO E. TAYLOR (*J. Biol. Chem.*, 1909, 5, 381—388. Compare Abstr., 1907, i, 665).—Another successful experiment is recorded on the synthesis of a small amount of a protamine by means of tryptic action on the purified amino-acids separated from salmine.  
W. D. H.

**Electrical Migration of Enzymes.** VICTOR HENRI (*Biochem. Zeitsch.*, 1909, 16, 473—474).—Polemical (compare Michaelis, this

vol., i, 277). The author has previously described an apparatus for the investigation of the electric migration of a number of enzymes. Stress is laid on the importance of first dialysing the enzyme solutions and controlling the freedom from electrolytes by conductivity measurements. Pancreas amylase alone migrates to the cathode; all other enzymes go to the anode.

E. F. A.

**Electrical Migration of Enzymes.** LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 16, 475).—Polemical. A reply to Henri (see preceding abstract.)

E. F. A.

**Electrical Migration of Enzymes. II. Trypsin and Pepsin.** LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 16, 486—488. Compare preceding abstracts).—Trypsin, in  $\frac{1}{2}\%$  solution, after dialysis for twenty-four hours, was placed as the middle element of a cell having silver in sodium chloride as anode and zinc in zinc sulphate as cathode, and the current passed for twenty-four hours. In this time the enzyme migrates almost entirely to the anode. It behaves similarly in weak alkaline solution, but when the solution is made distinctly acid, the enzyme migrates to the cathode. The addition of sodium chloride to the neutral solution does not disturb the normal anode migration. The undialysed enzyme migrates mainly to the anode, but at the same time, to a slight extent, towards the cathode. These observations are in agreement with the amphoteric character of trypsin, in which, further, the electro-negative properties preponderate. Pepsin, either in neutral or acid solution, migrates to the anode. This, also, is in agreement with its strongly electro-negative character.

E. F. A.

**Are Pepsin and Rennin Identical?** ALONZO E. TAYLOR (*J. Biol. Chem.*, 1909, 5, 399—404).—The theory that these two enzymes are identical cannot be proved by quoting Ehrlich's side-chain theory; its application to enzyme action is regarded as arbitrary and devoid of experimental basis.

It is possible to prepare a pepsin which has no rennetic properties, and to prepare a rennin without peptic properties. The data are best interpreted as indicating that the two enzymes are different substances.

In cancer of the stomach in man, rennet disappears at an early stage, but the gastric juice still digests protein.

W. D. H.

**Fermentative Cleavage of Polypeptides. VII.** EMIL ABDERHALDEN, G. CAEMMERER, and LUDWIG PINCUSOHN (*Zeitsch. physiol. Chem.*, 1909, 59, 293—319. Compare Abstr., this vol., i, 275).—The present paper records a number of experiments on the influence of certain salts on the activity of peptolytic enzymes. Potassium cyanide, 1 in 50,000, has no effect; greater concentrations accelerate the cleavage until the concentration of 1% inhibits the action. Sodium fluoride has also an inhibiting effect, but in low concentrations accelerates. Magnesium sulphate has little or no effect, but magnesium chloride in high concentration is inhibitory; calcium chloride accelerates, but

strontium chloride is indifferent. The addition of glycerol or of *d*-, *l*-, and *dl*-alanine is inhibitory to the fermentation cleavage of *dl*-leucylglycine and of glycyl *l*-tyrosine by yeast juice; *d*-alanine is most active in this direction, especially at the temperature of 45°.

W. D. H.

**Animal Invertins and Lactases. Their Specific Action.** H. BERRY (*Compt. rend.*, 1909, 148, 949—952).—A discussion of the results of work published elsewhere (*Compt. rend. Soc. Biol.*, 1906, 1908). Experiments have been carried out on the hydrolytic action of certain animal ferments on sucrose, raffinose, gentianose, stachyose, lactose, lactobionic acid, lactosazone, and lactose-carbamide. The ferments employed were obtained by extraction of the small intestine of dogs or fetal calves and the gastro-intestinal sac of the lobster and *Aplysia punctata*.

It is probable that the invertin obtained from the intestine of dogs is different from that secreted by the gastro-intestinal sac of molluscs. For invertins of this type, which bring about the separation of lævulose from sugars, the author proposes the name "lævulo-polyase." The gastro-intestinal sac of snails is capable of hydrolysing lactose, lactosazone, and lactobionic acid with formation of galactose. For diastases of this type, the name "lacto-bionase" is suggested. There are probably several species of diastases.

W. O. W.

**The Influence of Magnesia on the Inversion of Sucrose [by Invertase] at Different Temperatures.** J. TRIBOT (*Compt. rend.*, 1909, 148, 788—790. Compare this vol., i, 73).—Experiments were made with impure invertase with and without the addition of magnesia, and with invertase purified by twelve successive precipitations and leaving no perceptible residue on ignition. At temperatures above 30°, the action was somewhat accelerated by the presence of magnesia, and was much more rapid where impure invertase was used than where the invertase had been purified.

E. J. R.

**Inversion of Sucrose and Maltose by Ferments.** ALONZO E. TAYLOR (*J. Biol. Chem.*, 1909, 5, 405—408).—The results given confirm those of Hudson, that the inversion of sucrose, and probably of maltose, follows the course of a unimolecular reaction. This is contradictory to the statements of Mlle. Piloche (*J. Chim. Phys.*, 1908, 6, 229), but a recalculation of her results show they are not always regular; the reasons for the variations are not at present clear.

W. D. H.

**Critical Hydroxyl Ion Concentrations in Diastatic Hydrolysis.** CLARENCE QUINAN (*J. Biol. Chem.*, 1909, 6, 53—63).—Diastase obtained from three different sources maintains a constant relation to equivalent solutions of sodium carbonate and hydroxide. Evidence is adduced which makes it probable that the diastase concentration of the pancreatic juice very greatly exceeds that of saliva. Diastase is shown to be a very delicate indicator of the presence of free hydroxyl ions. It is possible to make a sharp quantitative distinction between various fluids containing diastase in terms of decinormal sodium hydroxide.

W. D. H.

**Ionic Potentials of Salts and their Power of Inhibiting Lipolysis.** R. H. NICHOLL (*J. Biol. Chem.*, 1909, 5, 453—468).—The power of the nitrates of various metals to inhibit the action of lipase on ethyl butyrate is a function chiefly of the energy content or ionic potential of the cations. This confirms Mathew's hypothesis on the subject.  
W. D. H.

**New Analogies between Natural and Artificial Oxydases.** JULES WOLFF (*Compt. rend.*, 1909, 148, 946—949. Compare this vol., i, 279).—The paper contains details of experiments on the action of easily hydrolysable salts, which, in the presence of natural or artificial oxydases, appear to behave as co-enzymes in promoting the oxidation of certain substances, such as quinol, catechol, cochineal, orcinol, and the sulphonic acids of alizarin and orcinol. The salts examined included manganous acetate and the phosphates and citrates of sodium. Colloidal ferrous ferrocyanide was employed as the artificial oxydase, and was found to behave in the same way as Bertrand's laccase extracted from lucerne. The following are the chief conclusions arrived at: (1) Traces of dibasic phosphates accelerate oxidation, whilst larger quantities retard it. (2) Monobasic phosphates have no action. (3) Neutralisation of the alkalinity in the case of the phosphate stops the oxidation, which re-commences on the addition of fresh dibasic phosphate. (4) There is an optimum concentration of phosphate corresponding with a definite amount of enzyme. (5) Tribasic citrates behave as dibasic phosphates, but the acid citrates exert a paralysing influence on the oxidation.  
W. O. W.

**Preparation of Arsenophenols.** FARBERWERKE VORM. MEISTER LUCIUS & BRÜNING (D.R.-P. 206456).—Arsenophenol,  $\text{As}_2(\text{C}_6\text{H}_4\cdot\text{OH})_2$ , a yellowish-brown powder, decomposing above  $200^\circ$ , is obtained by reducing sodium hydroxyphenylarsinate with a solution of sodium hyposulphite, sodium hydroxide, and magnesium chloride; its alkali derivative is soluble in water, and is precipitated therefrom by alcohol.

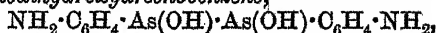
*Arseno-o-cresol*,  $\text{As}_2(\text{C}_6\text{H}_3\text{Me}\cdot\text{OH})_2$ , is similarly prepared from 4-hydroxy-*m*-tolylarsinic acid.  
F. M. G. M.

**Preparation of Derivatives of Phenylarsenious Oxide and Arsenobenzene.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 206057).—*p*-Aminophenylarsinic acid and its derivatives containing quinquivalent arsenic are reduced to derivatives containing this element in the tervalent condition, the products being far more toxic towards trypanosomes, either *in vitro* or *in vivo*, than are the organic derivatives of arsenic acid.

*4-Aminophenylarsenious oxide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}\cdot 2\text{H}_2\text{O}$ , white needles or leaflets, evolving water at  $80^\circ$  and frothing at  $100^\circ$ , is produced by reducing 4-aminophenylarsinic acid with hydriodic and sulphurous acids, or with phenylhydrazine.

*4:4'-Diaminoarsenobenzene*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , pale yellow flakes, m. p.  $139\text{--}140^\circ$ , insoluble in water and the ordinary organic media, is produced by reducing atoxyl with stannous chloride.

*4:4'-Diaminodihydroxyarsenobenzene*,



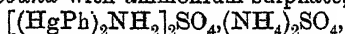
pale yellow flakes, m. p. 227°, are obtained by reducing 4-amino-phenylarsenious oxide with sodium amalgam in methyl-alcoholic solution.

Phenylglycinearsinic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}(\text{OH})_2$ , when reduced with alkaline sodium hyposulphite, gives rise to *arsenophenylglycine*,  $\text{As}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , reddish-brown powder, soluble in aqueous sodium carbonate, but insoluble in dilute mineral acids and the ordinary organic media.

*Oxalyl-p-aminophenylarsinic acid*, white, crystalline powder, melting above 360°, is prepared by heating atoxyl with oxalic acid; when reduced with sodium hyposulphite, it yields *arseno-oxanic acid*,  $\text{As}_2(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{H})_2$ , a pale yellow precipitate, insoluble in organic solvents, but dissolving in aqueous alkalis. F. M. G. M.

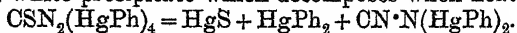
**New Organic Mercury Compounds.** LEONE PESCI (*Gazzetta*, 1909, 39, i, 147—154).—Salts of mercuriphenyl react with ammonia to form compounds of phenylmercuriammine,  $[(\text{HgPh})_2\text{NH}_2]'$ . Alkalis or silver oxide do not yield the hydroxide, but decompose the salts with evolution of ammonia.

*Phenylmercuriammine acetate* crystallises from methyl alcohol in needles, m. p. 179°; it dissolves readily in alcohol, but sparingly in water. The *nitrate* crystallises from alcohol in brilliant scales, m. p. 230—235° (decomp.); the *sulphate* forms a crystalline, infusible precipitate, which forms a *compound* with ammonium sulphate,



crystallising in rectangular tablets. The *chloride* separates from water in microscopic prisms, m. p. 184° (decomp.).

The acetate reacts with carbon disulphide in alcoholic solution, forming mercury diphenyl:  $(\text{HgPh})_2\text{NH}_2\cdot\text{C}_2\text{H}_3\text{O}_2 + \text{CS}_2 = \text{HgPh}_2 + \text{HgS} + \text{C}_2\text{H}_4\text{O}_2 + \text{CNSH}$ . Thiocarbamide forms a white, amorphous *compound*,  $\text{CSN}_2(\text{HgPh})_4$ , darkening at 104—105°, insoluble in ordinary solvents:  $(\text{HgPh})_2\text{NH}_2\cdot\text{C}_2\text{H}_3\text{O}_2 + \text{CS}(\text{NH}_2)_2 = \text{CSN}_2(\text{HgPh})_4 + 2\text{NH}_4\cdot\text{C}_2\text{H}_3\text{O}_2$ . Boiling alcohol decomposes this compound, yielding mercuric sulphide, mercury diphenyl, and *mercuriphenylcyanamide*, an amorphous, white precipitate which decomposes when heated:



Diphenylthiocarbamide and phenylmercuriammine acetate yield mercuric sulphide, mercury diphenyl, and diphenylguanidine. *p*-Ditolylthiocarbamide reacts similarly.

C. H. D.

## Organic Chemistry.

**Electron Conception of Valency in Organic Chemistry.**  
 JOHN M. NELSON and K. GEORGE FALK (*School of Mines Quart.*, 1909, 30, 179—198).—J. J. Thomson (*Corpuscular Theory of Matter*, 1907) has suggested that the valency of an element depends on the number of electrons which can be transferred to or from an atom of the element by the action of the atoms of other elements. On this view the valency lines, being tubes of electric force, are supposed to have direction, the direction of transfer of the (negative) electron being indicated by an arrow. In methane, for example, the four lines are directed towards the carbon, in carbon tetrachloride away from the carbon, the difference between the two extreme states of carbon being eight electrons. The authors have extended these considerations to a number of organic compounds, and explain the existence of a number of geometrical isomerides without taking into account spatial relations.

In the case of ethane, one carbon atom has a charge of four, the other of two, negative electrons, so that one methyl group is regarded as being positively charged compared with the other. The behaviour of triphenylmethyl as an electrolyte may be accounted for on similar lines, in solution  $C(C_6H_5)_3$  ions, positive and negative, being present.

For compounds containing double or triple linkings, the direction of the valencies may, to some extent, be deduced from the behaviour of the compound. From the additive reactions of propylene the conclusion is drawn that compounds of the type  $R_2C:CR_2$  exist in the form  $R_2C \rightleftharpoons CR_2$ . Of the isomeric substances of type  $RR'C:RR'$ , the stable have the formula  $RR'C \rightleftharpoons CRR'$ ; the unstable,  $RR'C \rightleftharpoons CRR'$ . In the case of cinnamic acid, there are three possibilities,  $PhCH \rightleftharpoons CH \cdot CO_2H$ ,  $PhCH \rightleftharpoons CH \cdot CO_2H$ , and  $PhCH \rightleftharpoons CH \cdot CO_2H$ , which may correspond with the three known isomerides. The formula for benzene and the representation of compounds with triple linkings are also considered.

The difference between the two extreme states of nitrogen (from ammonia to nitric acid) is eight electrons; between that in ammonia,  $N \rightleftharpoons H_3$ , and nitrous acid,  $O \rightleftharpoons N \rightarrow O \leftarrow H$ , six electrons. Hydrazine is thus represented  $H_2 \rightleftharpoons N \rightarrow N \rightleftharpoons H_2$ , which accounts for the apparent difference in the behaviour of the nitrogens. As regards the diazo-compounds, reasons are given for the assignation of the following

$$R-N \equiv N$$

formulæ :  $\downarrow$  for diazonium salts,  $R-N \rightleftharpoons N \cdot X$  for *syn*-compounds, and  $R \cdot N \rightleftharpoons N \cdot X$  for *anti*-compounds.

The representation of isomeric ketones and oximes is also discussed.  
 G. S.

**$\gamma$ -Methylheptane.** LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1909, 31, 558—561).—In continuation of a study of the octanes (this vol., i, 125, VOL. XCVI. i.

and earlier abstracts),  $\gamma$ -methylheptane has been prepared. This hydrocarbon has previously been obtained in an impure state by Welt (Abstr., 1895, ii, 97) by treating a mixture of amyl and ethyl iodides with sodium.

When methyl *n*-butyl ketone, obtained by the hydrolysis of ethyl *n*-propylacetoacetate, is treated with magnesium ethyl bromide,  $\gamma$ -methyl- $\gamma$ -heptanol,  $\text{CH}_2\text{Me}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\text{Pr}^a$ , b. p. 161—162°/763 mm., is produced as a colourless liquid with a eucalyptus-like odour. On converting this compound into the corresponding iodide and reducing the latter,  $\gamma$ -methylheptane,  $\text{CH}_2\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\text{Pr}^a$ , b. p. 117·6°/760 mm., is obtained as a colourless, mobile liquid, which has  $D_{15}^{25}$  0·7167 and  $n_D^{25}$  1·4022. The hydrocarbon attacks mercury with formation of a black substance.

E. G.

**Diisobutyl or  $\beta$ -Dimethylhexane.** LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1909, 31, 585—590).—The values assigned to the physical constants of  $\beta$ -dimethylhexane by different observers show considerable variation. The synthesis of the hydrocarbon has therefore been carried out by two distinct methods, and the product carefully purified.

The first method consists in treating isobutyl iodide with sodium, whilst the second is as follows. Methyl isoamyl ketone, prepared by the hydrolysis of ethyl isobutylacetoacetate, is treated with magnesium methyl iodide, and  $\beta$ -dimethyl- $\beta$ -hexanol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^b$ , b. p. 152—154°/760 mm., is thus obtained. This compound is converted into the corresponding iodide, which, on reduction, yields  $\beta$ -dimethylhexane as a colourless, mobile liquid with a pleasant odour. The hydrocarbon obtained by the first method had b. p. 108—108·3°/760 mm.,  $D_{15}^{25}$  0·6989, and  $n_D^{25}$  1·3926, whilst that obtained by the second method had b. p. 108·3—108·5°,  $D_{15}^{25}$  0·6993, and  $n_D^{25}$  1·3935. The first method is the quicker and simpler, but the second yields a purer product.

E. G.

**Preparation of Pure Ethyl Alcohol.** W. PLÜCKER (*Zeitsch. Nahr. Genussm.*, 1909, 17, 454—458).—Of the many methods which have been proposed for the preparation of pure ethyl alcohol, the one which yields the best results consists in boiling the alcohol under a reflux apparatus for about ten hours after the addition of about 7% of sodium hydroxide; the alcohol is then distilled from the alkali. Metallic calcium affords the best means of dehydrating alcohol.

W. P. S.

**Derivatives of the Amyl Alcohols from Fusel Oil.** V. WILLY MARCKWALD and ERNST NOLDA (*Ber.*, 1909, 42, 1583—1594. Compare Abstr., 1904, i, 362).—The tendency to the formation of mixed crystals, which is shown by mixtures of derivatives of *d*-amyl alcohol and isoamyl alcohol (*loc. cit.*), is still more pronounced in the case of derivatives of *d*- and of *l*-amyl alcohols. Since the latter is unknown, the experiments have been performed with derivatives of the purest obtainable commercial (95%) *d*-amyl alcohol and of *r*-amyl alcohol prepared from formaldehyde and magnesium *sec*-butyl bromide.

The freezing-point curve of a  $\psi$ -racemic mixture is generally a

horizontal straight line. This is shown to be the case with *d*- and *r*-1-amyl 3-nitrophthalates, the m. p. of the esters and of their mixtures being 116°; with *d*- and *r*-2-amyl 3-nitrophthalates, m. p. 155°, and with *d*- and *r*-amyl phenylcarbamates, m. p. 31°. The solubility curve of aqueous solutions of the barium salts of *d*- and *r*-amyl-sulphuric acids is also rectilinear. The freezing-point curve of a  $\psi$ -racemic mixture may, however, show a maximum or a minimum. The only recorded case of the first kind is Adriani's carboximes (Abstr., 1900, ii, 462). The authors have discovered the first instance of the second type in the amyl carbamates. Mixtures of *d*-amyl carbamate, m. p. 62.2° (not 61°: *loc. cit.*) and *r*-amyl carbamate, m. p. 51.3°, form an unbroken series of mixed crystals, and the m. p. curve, which is neither parabolic nor hyperbolic, shows a minimum. *d*- and *r*- $\beta$ -Methylvaleramides,  $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , which contain an atom of oxygen less than the preceding carbamates, do not exhibit the same behaviour; the amides and also their mixtures have the same m. p., 126°. The active amide is obtained by converting *d*-amyl iodide into the nitrile,  $\text{C}_5\text{H}_{11}\cdot\text{CN}$ , b. p. 152°,  $D_{19}^{25}$  0.8077,  $[\alpha]_D + 7.62^\circ$ , which is changed by concentrated hydrochloric acid into the amide. *r*- $\beta$ -Methylvaleramide and the isomeric *isohexoamide*,  $\text{CH}_2\text{Pr}^s\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 119°, form a series of mixed crystals, and the m. p. curve is parabolic. The preceding active amide yields on hydrolysis by 70% sulphuric acid at 110° *d*- $\beta$ -methylvaleric acid, identical with Neuberg and Rewald's *d*-hexoic acid (Abstr., 1908, i, 310; compare also Hardin and Sikorsky, *ibid.*, ii, 470).

The problem of racemisation during chemical transformations has been attacked. Pure *d*-amyl alcohol and hydrogen bromide yield *d*-amyl bromide,  $[\alpha]_D + 3.68^\circ$ . Commercial 95% *d*-amyl alcohol and phosphorus tribromide yield *d*-amyl bromide,  $[\alpha]_D + 4.05^\circ$ , or  $4.25^\circ$  allowing for the presence of 5% of *iso*amyl bromide. *d*-Amyl alcohol, having  $\alpha_D - 2.29^\circ$  in a 0.5 dcm. tube, is converted into *d*-amyl bromide, which is changed by silver acetate at 150° into *d*-amyl acetate, the hydrolysis of which by 22% sodium hydroxide for twenty-two hours yields *d*-amyl alcohol having  $\alpha_D$  only  $-1.08^\circ$ . The racemisation is not due to the hydrolysis of the acetate, because *d*-amyl acetate, prepared from the alcohol and acetic acid, regenerates by hydrolysis under the same conditions *d*-amyl alcohol of unchanged rotation  $-2.29^\circ$ . The proof that the racemisation occurs during the action of the silver acetate on the bromide is furnished by converting the bromide by alcoholic sodium iodide into the more reactive iodide, and converting the latter by alcoholic potassium acetate into *d*-amyl acetate, which by hydrolysis yields *d*-amyl alcohol,  $\alpha_D - 2.13^\circ$  (0.5-dcm. tube). When the iodide is treated with silver acetate, the *d*-amyl alcohol finally obtained has  $\alpha_D - 1.53^\circ$ , whilst the alcohol obtained directly from the iodide by moist silver oxide has  $\alpha_D - 1.49^\circ$ .  
C. S.

**Reductions with Sodium Amyloxyde.** OTTO DIELS and RICHARD RHODIUS (*Ber.*, 1909, 42, 1072—1076).—Sodium amyloxyde acts as an active reducing agent, being itself converted into *isovaleric* acid and other compounds. Benzylideneaniline is easily converted into benzylaniline. Azobenzene is reduced within a few minutes to hydrazo-

benzene, *iso*amylaniline being also formed, possibly owing to the condensation of *isovaleraldehyde* to a Schiff's base, which is subsequently hydrated. When the reduction is prolonged, *iso*amylaniline is the sole product. Cinnamic acid is reduced to phenylpropionic acid.

Indigotin is instantly converted into a yellow product; anthraquinone yields oxanthranol, which is reconverted into indigotin on exposure to air; benzophenone forms benzhydrol.

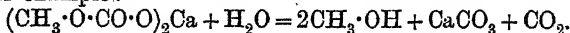
The superior reducing activity of a mixture of sodium and amyl alcohol to one of sodium and ethyl alcohol is usually attributed to the higher reaction temperature in the former case. That this is not the case is indicated by the fact that benzophenone is not reduced by sodium ethoxide at 140°, but easily reduced by sodium amyloxide at 90°.

E. F. A.

**The Scission of Sugars. IV. The Electrolysis of Glycerol and Glycol.** WALTHER LÖB and GEORG PULVERMACHER (*Biochem. Zeitsch.*, 1909, 17, 343—355).—Glycerol, on subjection to electrolysis in 5% sulphuric acid with cooled lead anodes, yielded formaldehyde, formic acid, non-volatile acids, of which the calcium salts contained from 19—26% calcium, and a pentose. Similar results were obtained by direct oxidation of glycerol with lead peroxide. Glycol, under similar conditions of electrolysis, yielded formaldehyde, formic and carbonic acids, and non-volatile acids, which have not been identified.

S. B. S.

**Union of Carbon Dioxide with Alcohols, Sugars, and Hydroxy-acids.** MAX SIEGFRIED and S. HOWWJANZ (*Zeitsch. physiol. Chem.*, 1909, 59, 376—404).—Experiments have shown that when carbon dioxide is led at 0° into milk of lime containing aliphatic hydroxy-derivatives, a certain amount of the dioxide combines with the hydroxy-compound. This is proved by the fact that the filtrate when kept, or when warmed, deposits calcium carbonate, and that the amount of this carbonate is constant within certain limits for each hydroxy-compound. The phenomena are not due to the formation of a colloidal solution of calcium carbonate, since in the presence of an excess of calcium hydroxide the solution is first alkaline, but, on standing, becomes distinctly acid. The hydroxy-derivatives combine with the carbon dioxide, yielding acids, for example:  $\text{CH}_3\cdot\text{OH} \rightarrow \text{CH}_3\cdot\text{O}\cdot\text{CO}\cdot\text{OH}$ , which are converted into calcium salts. These salts are soluble, but when their solutions are kept or heated, decomposition occurs, for example:



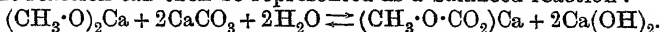
The calcium salts of *glycerolcarbonic acid* and of *ethyleneglycolcarbonic acid* have been prepared. The analytical data for the former agree fairly well with the formula  $\text{OH}\cdot\text{CH}_2\cdot\text{CH} \begin{matrix} \text{O}\cdot\text{CO} & \text{O} \\ \diagdown & \diagup \\ \text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{O} \end{matrix} \text{Ca}$ , and

for the latter with the formula  $\begin{matrix} \text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{O} \\ \diagdown & \diagup \\ \text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{O} \end{matrix} \text{Ca}$ .

Precipitated calcium carbonate does not react with hydroxy-derivatives, except in the presence of the calcium hydroxide, and it is possible that the hydroxyl derivative reacts with the calcium

hydroxide, forming a compound of the type  $(\text{CH}_3\cdot\text{O})_2\text{Ca}$ , the hydrolysis of which is prevented to a large extent by the excess of alkali present.

The reaction can then be represented as a balanced reaction :



The reaction  $2\text{CH}_3\cdot\text{OH} + \text{Ca}(\text{OH})_2 + 2\text{CO}_2 = (\text{CH}_3\cdot\text{O}\cdot\text{CO}_2)\text{Ca} + 2\text{H}_2\text{O}$  also takes place to a certain extent.

The following compounds combine with carbon dioxide: methyl, ethyl, propyl, butyl, *isobutyl*, *tert.*-butyl, and benzyl alcohols. Ethylene glycol, glycerol, erythritol, quercitol, mannitol, dulcitol, *l*-arabinose, xylose, dextrose, *l*ævulose, *d*-galactose, sucrose, lactose, maltose, hydroxyacetic acid,  $\alpha$ -lactic acid, paralactic acid, hydroxy*iso*-butyric acid. The ratio  $\text{CO}_2/\text{substance}$  has been determined in each case. The value is less than unity in the case of monohydroxy-derivatives, owing to the reversible nature of the reaction. J. J. S.

**Oxonium Dibromides of Simple Ethers and their Constitution.** WLADIMIR W. TSCHELINZEFF and W. K. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 131—145; *Ber.*, 1909, 42, 1531—1540).—The authors have investigated the properties and transformations of the compounds formed by bromine with ethyl and *isoamyl* ethers.

The former compound has in freezing acetic acid a molecular weight corresponding with the composition,  $\text{Et}_2\text{OBr}_2$ , McIntosh's views (*Trans.*, 1905, 87, 784) concerning the constitution of this compound hence being inaccurate. The compound has  $D_4^{25}$  1.7647,  $D_4^{15}$  1.7168,  $D_4^{17}$  1.6644,  $n_D$  1.496. Taking for the oxygen atom of the compound the same atomic refraction as is possessed by hydroxyl oxygen, the molecular refraction is calculated to be 39.80, the actual value being 41.07; the difference is accounted for by oxonium oxygen having a different atomic refraction from hydroxyl oxygen, and by the influence exerted on the refraction by the bromine atoms in the dibromide. With magnesium ethyl iodide, the compound gives butane:  $\text{Et}_2\cdot\text{O}:\text{Br}_2 + 2\text{MgEtI} = \text{Et}_2\text{O} + 2\text{MgBrI} + \text{C}_4\text{H}_{10}$ , the compound  $\text{Et}_2\cdot\text{O}:\text{Br}_2$  being probably an intermediate product. Similarly, with magnesium propyl iodide, hexane is obtained.

The heat of formation of  $\text{Et}_2\text{OBr}_2$  from its constituents at  $20^\circ$  is 9.13 cal., and that of the corresponding compound of *isoamyl* ether,  $(\text{C}_5\text{H}_{11})_2\text{OBr}_2$ , 8.75 cal. The velocities of formation and of decomposition by water have been measured.

Of the various structural formulæ possible for these compounds, the authors give preference to  $\begin{array}{c} \text{R} > \text{O} < \begin{array}{c} \text{Br} \\ | \\ \text{Br} \end{array} \end{array}$  or  $\begin{array}{c} \text{R} > \text{O} < \begin{array}{c} \text{Br} \\ || \\ \text{Br} \end{array} \end{array}$ . T. H. P.

**Derivatives of Monohalogenated Ethers.** D. GAUTHIER (*Ann. Chim. Phys.*, 1909, [viii], 16, 289—358).—In a preliminary paper (*Abstr.*, 1907, i, 20) the author has described the method of preparation of alkyloxy-nitriles of the type  $\text{RO}\cdot\text{CH}_2\cdot\text{CN}$  (compare also Sommelet, *Abstr.*, 1907, i, 21) by the action of cuprous cyanide and Henry's chloromethyl alkyl ethers,  $\text{RO}\cdot\text{CH}_2\text{Cl}$ ; the investigation has been extended to alkyloxy-nitriles of the type  $\text{RO}\cdot\text{CHMe}\cdot\text{CN}$ , and the extensive series of derivatives described in the original may be conveniently considered under the following headings: (i) alkyloxy-nitriles of the type

$\text{RO}\cdot\text{CH}_2\cdot\text{CN}$ , and the corresponding amides, acids, and esters; (ii) chloroethyl alkyl ethers of the type  $\text{RO}\cdot\text{CHMeCl}$ , and the corresponding nitriles, amides, acids, and esters; (iii) alkyloxyketones of the type  $\text{RO}\cdot\text{CHR}'\cdot\text{CO}\cdot\text{R}''$ , obtained from the nitriles by means of the Grignard reaction; (iv) imino-ketones of the type  $\text{RO}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}'$ , obtained by the condensation of the nitriles with methyl ketones in the presence of sodium; (v) ethers of acetylenic glycols of the type  $\text{RO}\cdot\text{CHR}'\cdot\text{C}\equiv\text{C}\cdot\text{CHR}''\cdot\text{OR}$ , obtained from the chloro-alkyl ethers by condensation with acetylenic organomagnesium compounds; and the products derived from these compounds by the action of bromine, hydrogen, or sodium alkoxides.

A list of the compounds described under the several headings is appended.

(i) Ethoxyacetonitrile (compare Sommelet, Abstr., 1907, i, 21), b. p.  $131-132^\circ/732$  mm.,  $D_4^{20}$  0.9077,  $n_D^{20}$  1.388; methoxyacetonitrile (*loc. cit.*) has  $D_4^{20}$  0.9373,  $n_D^{20}$  1.380: the *amide* has m. p.  $92^\circ$ ; propoxyacetonitrile (*loc. cit.*) has  $D_4^{20}$  0.896,  $n_D^{20}$  1.401: the *amide* has m. p.  $63^\circ$ ; isobutoxyacetonitrile has  $D_4^{20}$  0.873,  $n_D^{20}$  1.404; isobutoxyacetic acid,  $\text{C}_4\text{H}_9\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , has b. p.  $216^\circ/730$  mm.: the *amide* has m. p.  $76^\circ$ ; isoamyloxyacetonitrile (*loc. cit.*) has  $D_4^{20}$  0.877,  $n_D^{20}$  1.414.

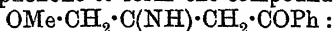
(ii) The following chloroethyl alkyl ethers were prepared by the action of hydrochloric acid on a mixture of the alcohol and paraldehyde:  $\beta$ -Chloroethyl propyl ether,  $\text{C}_3\text{H}_7\text{O}\cdot\text{CHClMe}$ , b. p.  $112-115^\circ/731$  mm.;  $\beta$ -chloroethyl isobutyl ether,  $\text{C}_4\text{H}_9\text{O}\cdot\text{CHClMe}$ , b. p.  $132-138^\circ/731$  mm.;  $\beta$ -chloroethyl isoamyl ether,  $\text{C}_5\text{H}_{11}\text{O}\cdot\text{CHClMe}$ , b. p.  $162-165^\circ/721$  mm.; these ethers react with cuprous cyanide to yield the corresponding nitrile, and the following compounds were thus prepared:  $\alpha$ -ethoxypropionitrile (compare Colson, Abstr., 1899, i, 251), b. p.  $129-130^\circ/730$  mm.,  $D_4^{16}$  0.878,  $n_D^{16}$  1.390;  $\alpha$ -methoxypropionitrile,  $\text{OMe}\cdot\text{CHMe}\cdot\text{CN}$ , b. p.  $118^\circ/729$  mm.,  $D_4^{20}$  0.893,  $n_D^{20}$  1.382: the *amide*, m. p.  $81^\circ$ ;  $\alpha$ -propoxypropionitrile,  $\text{C}_3\text{H}_7\text{O}\cdot\text{CHMe}\cdot\text{CN}$ , b. p.  $150^\circ/727$  mm.,  $D_4^{20}$  0.866,  $n_D^{20}$  1.398;  $\alpha$ -isobutoxypropionitrile,  $\text{C}_4\text{H}_9\text{O}\cdot\text{CHMe}\cdot\text{CN}$ , b. p.  $155-158^\circ/721$  mm.,  $D_4^{20}$  0.848,  $n_D^{20}$  1.402.

(iii) isoButoxypropanone,  $\text{C}_4\text{H}_9\text{O}\cdot\text{CH}_2\cdot\text{COMe}$ , b. p.  $157^\circ/730$  mm.; isoamyloxypropanone,  $\text{C}_5\text{H}_{11}\text{O}\cdot\text{CH}_2\cdot\text{COMe}$ , b. p.  $179-181^\circ/730$  mm.;  $\alpha$ -methoxybutan- $\beta$ -one,  $\text{OMe}\cdot\text{CH}_2\cdot\text{COEt}$ , b. p.  $130-131^\circ/729$  mm.: the phenylhydrazone has b. p.  $170^\circ/18$  mm.;  $\alpha$ -methoxypentan- $\beta$ -one,  $\text{OMe}\cdot\text{CH}_2\cdot\text{COPr}$ , b. p.  $142-150^\circ/730$  mm.;  $\beta$ -methoxybutan- $\gamma$ -one,  $\text{OMe}\cdot\text{CHMe}\cdot\text{COMe}$ , b. p.  $114^\circ/727$  mm.: the phenylhydrazone forms yellow crystals, m. p.  $57^\circ$ ;  $\beta$ -ethoxybutan- $\gamma$ -one,  $\text{OEt}\cdot\text{CHMe}\cdot\text{COMe}$ , has b. p.  $128^\circ/727$  mm.;  $\beta$ -propoxybutan- $\gamma$ -one,  $\text{C}_3\text{H}_7\text{O}\cdot\text{CHMe}\cdot\text{COMe}$ , b. p.  $148-149^\circ/727$  mm.;  $\beta$ -methoxypentan- $\gamma$ -one,  $\text{OMe}\cdot\text{CHMe}\cdot\text{COEt}$ , b. p.  $133^\circ/729$  mm.;  $\beta$ -ethoxypentan- $\gamma$ -one,  $\text{OEt}\cdot\text{CHMe}\cdot\text{COEt}$ , b. p.  $145^\circ/727$  mm.

(iv) The imino-ketones prepared by the condensation of the alkyloxyacetonitriles in the presence of sodium were isolated in the form of their copper salts; the ketones themselves were not obtained in a state of purity; ethoxyacetonitrile condenses with (a) acetone to form the imino-ketone,  $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{COMe}$ , of which the copper salt has m. p.  $158^\circ$ : the copper salt of the methyl derivative,  $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CHMe}\cdot\text{COMe}$ , is also described; with (b) methyl ethyl ketone to form the imino-ketone,  $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{COEt}$ ,

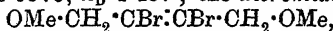
the copper salt of which has m. p. 135°; with (c) acetophenone to form the imino-ketone,  $\text{OEt}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\cdot\text{COPh}$ , of which the copper salt is described.

Methoxyacetoneitrile condenses with (a) acetone to form the compound  $\text{OMe}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CH}_2\text{COMe}$ , isolated in the form of its copper salt; with (b) acetophenone to form the compound

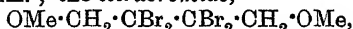


the copper salt has m. p. 190°.

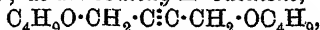
(v)  $\alpha\delta$ -Dimethoxy- $\Delta^{\beta}$ -butinene,  $\text{OMe}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OMe}$ , b. p. 158°/730 mm.,  $D_4^{25}$  0.9575,  $n_D^{25}$  1.437; the dibromide,



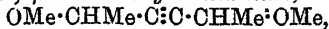
has b. p. 120°/16 mm.; the tetrabromide,



b. p. 162°/17 mm.;  $\alpha\delta$ -diethoxy- $\Delta^{\beta}$ -butinene,  $\text{OEt}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OEt}$ , has b. p. 179—180°/730 mm.,  $D_4^{25}$  0.9156,  $n_D^{25}$  1.435;  $\alpha\delta$ -dipropoxy- $\Delta^{\beta}$ -butinene,  $\text{C}_3\text{H}_7\text{O}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OC}_3\text{H}_7$ , b. p. 150°/20 mm.,  $D_4^{20}$  0.8916,  $n_D^{20}$  1.434;  $\alpha\delta$ -diisobutoxy- $\Delta^{\beta}$ -butinene,



b. p. 159—160°/20 mm.,  $D_4^{19}$  0.8739,  $n_D^{19}$  1.433;  $\alpha\delta$ -diisobutyloxy- $\Delta^{\beta}$ -butinene,  $\text{C}_5\text{H}_{11}\text{O}\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{OC}_5\text{H}_{11}$ , b. p. 190—192°/15 mm.,  $D_4^{18}$  0.8834,  $n_D^{18}$  1.445;  $\beta\epsilon$ -dimethoxy- $\Delta\gamma$ -hexinene,



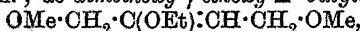
b. p. 160°/730 mm.,  $D_4^{19}$  0.8995,  $n_D^{19}$  1.428;  $\beta\epsilon$ -diethoxy- $\Delta\gamma$ -hexinene,  $\text{OEt}\cdot\text{CHMe}\cdot\text{C}:\text{C}\cdot\text{CHMe}\cdot\text{OEt}$ , b. p. 178—180°/730 mm.,  $D_4^{19}$  0.8944,  $n_D^{19}$  1.435.

On direct hydrogenation in the presence of reduced nickel, the above acetylenic ethers yield the corresponding saturated derivative; in order to obtain as large a surface of nickel as possible, the author adopted the expedient of coating glass beads, 2 mm. diameter, with nickel by shaking the slightly moist beads with nickel oxide, which was then reduced at 330°.  $\alpha\delta$ -Dimethoxybutane, b. p. 132—134°/733 mm. (compare Hamonet, Abstr., 1905, i, 403), obtained by reducing the corresponding butinene, was, at Bouveault's suggestion, converted into adipic acid by the successive action of carbon dioxide and water on the organomagnesium derivative,

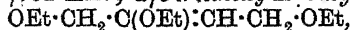


obtained from the  $\alpha\delta$ -dibromobutane prepared by the action of hydrobromic acid on the ether; sebamic acid was also obtained in the course of this reaction.  $\alpha\delta$ -Diethoxybutane,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OEt}$ , has b. p. 155—157°/730 mm.

By the action of sodium alkylxides on the ethers of acetylenic glycols, ethylenic ethers of the type  $\text{OR}\cdot\text{CH}_2\cdot\text{C}(\text{OR}')\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OR}$  were obtained, which on hydrolysis furnish diketones;  $\alpha\gamma\delta$ -trimethoxy- $\Delta^{\beta}$ -butylene,  $\text{OMe}\cdot\text{CH}_2\cdot\text{C}(\text{OMe})\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OMe}$ , has b. p. 179—180°/730 mm.;  $\alpha\delta$ -dimethoxy- $\gamma$ -ethoxy- $\Delta^{\beta}$ -butylene,



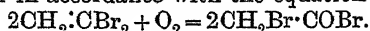
has b. p. 185—187°/732 mm.;  $\alpha\gamma\delta$ -triethoxy- $\Delta^{\beta}$ -butylene,



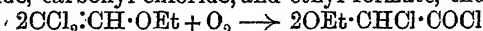
has b. p. 198—200°/729 mm.;  $\beta\epsilon$ -dimethoxy- $\delta$ -ethoxy- $\Delta\gamma$ -hexylene,  $\text{OMe}\cdot\text{CHMe}\cdot\text{C}(\text{OEt})\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OMe}$ , has b. p. 175—177°/730 mm.

M. A. W.

**Slow Oxidation of *as*-Dichlorovinyl Ethyl Ether.** WILLIAM FOSTER (*J. Amer. Chem. Soc.*, 1909, 31, 596—602).—Halogen derivatives of ethylene are capable of direct combination with oxygen with formation of acyl halides. Demole (*Abstr.*, 1878, 401, 847) has shown, for example, that *as*-dibromoethylene undergoes oxidation on exposure to the air in accordance with the equation



A study of the action of dry oxygen on *as*-dichlorovinyl ethyl ether, prepared by Neher and Foster's method (this vol., i, 202), has shown that this compound is slowly oxidised with formation of ethoxychloroacetyl chloride, carbonyl chloride, and ethyl formate, thus:



and  $\text{CCl}_2\text{:CH}\cdot\text{OEt} + \text{O}_2 \rightarrow \text{COCl}_2 + \text{H}\cdot\text{CO}_2\text{Et}$ . Small quantities of ethyl chloride also seem to be produced. The mechanism of the reaction is discussed.

*Ethoxychloroacetyl chloride*,  $\text{OEt}\cdot\text{CHCl}\cdot\text{COCl}$ , b. p. about  $150^\circ$  under ordinary atmospheric pressure, and  $53\text{--}54^\circ/11\text{ mm.}$ , is a clear, colourless, fuming liquid, which has  $D_4^{20} 1.2639$ . When treated with sodium ethoxide, it is converted into ethyl diethoxyacetate. E. G.

**Spontaneous Crystallisation of Chloroacetic Acid and its Mixtures with Naphthalene.** HENRY A. MIERS and FLORENCE ISAAC (*Proc. Roy. Soc.*, 1909, 82, A, 184—187\*).—Microscopic examination of crystals of chloroacetic acid obtained from fusion or solution has shown that there are three modifications,  $\alpha$ ,  $\beta$ , and  $\gamma$ , which melt respectively at  $61.5^\circ$ ,  $55^\circ$ , and  $50^\circ$ . The  $\alpha$ -form is the most stable, and the  $\gamma$ -form the least stable. The more stable modification crystallises with sharp edges in the solid mass of the less stable substance as if it were growing in a liquid.

The solubility and supersolubility curves of the three forms in water have been determined; the supersolubility curves are separated from each other by intervals of  $5^\circ$  to  $6^\circ$ .

Experiments with mixtures of chloroacetic acid and naphthalene have given no indication of the formation of mixed crystals, a result which is opposed to that obtained by Cady (*Abstr.*, 1899, ii, 405). The four curves representing the solubility of naphthalene in liquid chloroacetic acid and of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -chloroacetic acids in liquid naphthalene, as well as the corresponding supersolubility curves, have been determined. The diagrammatic representation of these curves shows that no less than eight freezing points may be exhibited by the fused mixture of the two substances. Each modification of a polymorphous substance possesses therefore a definite temperature of spontaneous crystallisation in its mixtures with another substance which is not polymorphous. H. M. D.

**Solidification of Mixtures of Water and *n*-Butyric Acid.** M. H. FAUCON (*Compt. rend.*, 1909, 148, 1189—1192. Compare this vol., i, 130).—The freezing-point curve of the system water-butyric acid has been studied. The eutectic mixture, separating at  $-13.4^\circ$ , has the molar composition  $\text{C}_4\text{H}_8\text{O}_2 + 0.70\text{H}_2\text{O}$ . No evidence has been obtained of the existence of definite hydrates. Above  $-3.8^\circ$ , butyric

\* and *Phil. Trans.*, 1909, A, 209, 337—377.

acid and water are miscible in all proportions; below this temperature, mixtures containing 25—60% of acid are not homogeneous.

W. O. W.

**Theory of Hydrolysis of Fats and Oils.** J. KELLNER (*Chem. Zeit.*, 1909, 33, 453. Compare Balbiano, Abstr., 1902, i, 450; 1903, i, 547; 1904, i, 216, 798; Lewkowitsch, Proc., 1899, 15, 190, Abstr., 1903, i, 225; and Marcusson, Abstr., 1906, i, 924).—It is shown that when palm kernel oil is hydrolysed by an alkali hydroxide under atmospheric pressure, the reaction is quadrimolecular, and no mono- or di-glyceride is formed as an intermediate product. When the hydrolysis is accomplished in an autoclave in presence of zinc oxide, the reaction tends to become bi- and ter-molecular by the formation of lower glycerides as intermediate products.

T. A. H.

**Oleic Acid.** WILHELM FAHRION (*Chem. Zeit.*, 1909, 33, 429).—The author calls attention to the occasional presence of unsaponifiable matters, saturated fatty acids (palmitic acid), and linoleic acid in commercial "Acid Oleic puriss."

L. DE K.

**Linolenic Acid of Linseed Oil.** ERNST ERDMANN and FRED BEDFORD (*Ber.*, 1909, 42, 1324—1333).—The results of the investigation show that linseed oil contains  $\alpha$ -linolenic acid, and that the solid hexabromide of this, on debromination, yields a mixture of  $\alpha$ - and  $\beta$ -linolenic acids, the second isomeride being characterised by yielding a liquid tetrabromide.

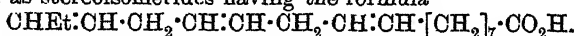
The mixed fatty acids of linseed oil, after removal of saturated acids by cooling to 0° and filtering, were found to distil for the most part unchanged at constant temperature under reduced pressure, and this method could not be used for their separation. The oleic acid was eliminated by converting the acids into their barium salts and treating these with a mixture of benzene, alcohol, and water, in which barium oleate is sparingly soluble. The mixture of acids, recovered from the barium salts, and now free from oleic acid, was esterified, and the quantity of hydrogen required for the complete reduction of the mixed esters by Sabatier and Senderens' catalytic process determined in a specially devised apparatus, described elsewhere (Bedford, *Inaug. Diss. Halle*, 1906). The sole product of the reduction was ethyl stearate, and the quantity of hydrogen absorbed indicated that in the mixture of esters used about 22% was ethyl  $\alpha$ -linolenate,  $C_{20}H_{34}O_2$ , and the rest ethyl linoleate,  $C_{20}H_{36}O_2$ .  $\alpha$ -Linolenic acid hexabromide, m. p. 179° (hexabromostearic acid), is readily prepared by adding bromine in small quantities to a well-cooled solution of the distilled, mixed fatty acids of linseed oil, separating the crystals, which form after twelve hours, and washing with ethyl acetate. The ethyl ester of the hexabromide, m. p. 151.5—152.5°, is crystalline, as is also the methyl ester, m. p. 157—158°.

When dissolved in alcohol and heated with zinc filings, the hexabromide is reduced, yielding a mixture of  $\alpha$ - and  $\beta$ -linolenic acids, b. p. 157—158°/0.001—0.002 mm. The ethyl ester of the hexabromide is reduced under similar conditions, yielding a mixture of the ethyl esters of  $\alpha$ - and  $\beta$ -linolenic acids, b. p. 132—133°/0.001 mm.

pressure,  $D_4^{20}$  0.8919,  $n_D^{20}$  1.46753,  $n_a^{20}$  1.46458,  $n_\beta^{20}$  1.47489. On reduction by Sabatier and Senderens' process, both the mixture of acids and the mixture of esters absorb the equivalent of six atoms of hydrogen, but on re-bromination, only a small proportion of the solid hexabromide (the additive product of the  $\alpha$ -acid or its ester) is formed, the residue in the product of the reaction being a liquid tetrabromide (the additive product of the  $\beta$ -acid or its ester) in each case.

T. A. H.

**Constitution of Linolenic Acid.** ERNST ERDMANN, FRED BEDFORD, and FRITZ RASPE (*Ber.*, 1909, 42, 1334—1346. Compare preceding abstract).—Investigation of the decomposition products of the ozonide peroxides of  $\alpha$ - and  $\beta$ -linolenic acids shows that the two acids must be regarded as stereoisomerides having the formula



The mixture of  $\alpha$ - and  $\beta$ -linolenic acids, obtained by the reduction of the hexabromide of the  $\alpha$ -acid (*loc. cit.*), when dissolved in hexahydro-toluene and treated with ozone at  $-20^\circ$ , yields an *ozonide*,  $\text{C}_{18}\text{H}_{30}\text{O}_{11}$ , in the form of a colourless, viscous oil. If chloroform be used as a solvent, an *ozonide peroxide*,  $\text{C}_{18}\text{H}_{30}\text{O}_{12}$ , of gummy consistence is formed. The ethyl ester prepared from the mixed acids also yields an *ozonide peroxide* under similar conditions (compare Harries and Thieme, *Abstr.*, 1906, i, 226, 793).

The ozonide peroxide of the ethyl esters, when treated with cold water, is decomposed readily to the extent of about one-third, and this portion is regarded as derived from  $\alpha$ -linolenic acid, whilst the residue, which decomposes when heated with water, is regarded as derived from the  $\beta$ -acid. The decomposition products in both cases are the same, namely, propaldehyde (*p*-nitrophenylhydrazone, m. p. 124—124.5°), malonic acid and the dialdehyde and semialdehyde corresponding to this, and ethyl hydrogen azelate with the corresponding semialdehyde. The carbon dioxide and acetaldehyde also formed are shown to be due to the decomposition of the malonic acid semialdehyde on heating.

T. A. H.

**Catalytic Actions of Colloidal Metals of the Platinum Group. V. Reduction of Fats.** CARL PAAL and KARL ROTH (*Ber.*, 1909, 42, 1541—1553. Compare *Abstr.*, 1908, i, 599).—It has been found possible completely to reduce castor oil, croton oil, olive oil, cotton seed oil, linseed oil, butter, and lard by repeating the treatment with palladium hydrosol and hydrogen a second time; sesamé oil and oleomargarin were not reduced completely. In all cases the volume of hydrogen required to effect complete reduction was greatly in excess of that calculated from the iodine values.

The product obtained from castor oil is a hard, white, crystalline mass, softening at  $78^\circ$ , m. p.  $81^\circ$ , which does not taste like the parent substance.

That derived from croton oil is a reddish-brown, hard fat, m. p.  $49$ — $51^\circ$ , which does not possess the characteristic physiological properties of croton oil. Olive oil yields a hard, white, crystalline mass, which softens at  $61^\circ$ , m. p.  $68.5^\circ$ . A white, brittle substance, m. p.

65—69°, having an iodine value 2, was obtained by reducing sesamé oil. Cotton seed oil yields an almost colourless and tasteless, hard, brittle substance, m. p. 56—60°. The product derived from linseed oil is a hard, white substance, m. p. 61—65°. Butter, when reduced completely, is converted into a white, fairly hard, brittle substance, which softens at 36°, m. p. 44°, tastes somewhat like cacao fat, and remains unaltered for several months. Lard is converted into an almost tasteless, hard, white tallow, m. p. 56—60°. The product (iodine value 1.2) obtained from oleomargarin is a white, brittle, crystalline, almost tasteless substance, which softens at 47°, m. p. 55°.

W. H. G.

**Preparation of Ether Esters.** M. H. PALOMAA (*Ber.*, 1909, 42, 1299—1302).—The methyl, ethyl, and propyl esters of methoxyacetic acid, when prepared by the action of the corresponding alkyl iodides on silver methoxyacetate, have b. p. 131.06—131.12°/763.1 mm., 143.9°/747.5 mm., and 165.2—165.4°/759.5 mm. respectively; these boiling points are in every case higher than those quoted by previous authors for samples prepared by the interaction of the sodium alkoxide with the esters of the chloro-substituted acids.

P. H.

**The Walden Inversion.** IV. EMIL FISCHER and HELMUTH SCHEIBLER (*Ber.*, 1909, 42, 1219—1228. Compare *Abstr.*, 1908, i, 857).—The object of this investigation was to ascertain whether the Walden-inversion is conditioned by the direct union of the carboxyl group with the asymmetric carbon atom. *l*- $\beta$ -Hydroxybutyric acid yields a dextrorotatory  $\beta$ -chlorobutyric acid, which, when treated with silver oxide and water, is reconverted into the original *l*- $\beta$ -hydroxybutyric acid. In this case, therefore, a Walden inversion does not take place, although it is possible, but very improbable, that a double inversion occurs.

*Methyl l*- $\beta$ -hydroxybutyrate,  $C_5H_{10}O_3$ , is a colourless oil, b. p. 67—68.5°/13 mm.; the corresponding *inactive* ester has b. p. 67—68°/12—13 mm. The active ester, when hydrolysed, yields *l*- $\beta$ -hydroxybutyric acid,  $[\alpha]_D^{20} - 14.1^\circ (\pm 0.1^\circ)$  in water (compare Magnus-Levy, *Arch. exp. Path. Pharm.*, 1901, 45, 390; McKenzie, *Trans.*, 1902, 81, 1411), and when treated with phosphorus pentachloride yields dextrorotatory *methyl*  $\beta$ -chlorobutyrate,  $C_5H_9O_2Cl$ , a colourless oil, b. p. 48—51°/13 mm.,  $[\alpha]_D^{20} + 21.96^\circ$  to  $+23.89^\circ$ . The latter substance, when hydrolysed with alkalis, is converted chiefly into crotonic acid, whilst with acids, it yields dextrorotatory  $\beta$ -chlorobutyric acid,  $C_4H_7O_2Cl$ , a white, crystalline solid, b. p. 99—100°/13 mm.,  $[\alpha]_D^{20} + 27.1^\circ$  in water containing an equivalent amount of sodium hydroxide,  $[\alpha]_D^{20}$  about  $+42^\circ$  in water. The active methyl  $\beta$ -chlorobutyrate, when boiled with water for about forty hours, is converted into *l*- $\beta$ -hydroxybutyric acid, although racemisation takes place to some extent during the reaction. The active  $\beta$ -chlorobutyric acid behaves in an analogous manner when treated with water and silver oxide at 37°.

W. H. G.

**Oxidation of Ethyl Glycollate by Mercuric Oxide.** HERMANN FLINGER (*J. pr. Chem.*, 1909, [ii], 79, 368).—Warm solutions of the hydrochloride of ethyl glycollate in water, alcohol, pyridine, and

other solvents are oxidised by yellow mercuric oxide, forming a red syrup which does not contain mercury and forms a red potassium salt. The investigation of the substance is being continued. C. S.

**Solubilities of the Oxalates of the Rare Earths. II. Solubility of Manganous Oxalate in Water, Ammonium Oxalate, Sulphuric or Oxalic Acid, and their Mixtures.** OTTO HAUSER and FRITZ WIRTH (*J. pr. Chem.*, 1909, [ii], 79, 358—368. Compare Abstr., 1908, ii, 778).—Fractional crystallisation of the double manganese nitrates affords a rapid method for the separation of the metals of the cerium group, but it is essential that the double salt and the solution should be free from the simple manganese salt. Contrary to statements in the literature, manganous oxalate is not easily soluble in dilute acids; the precipitate obtained by the addition of oxalic acid to an acid solution of salts of manganese and the metals of the cerium group always contains manganese. To find an explanation of this fact, the solubility of manganous oxalate at 25° in water, oxalic acid, ammonium oxalate, sulphuric acid, and mixtures of sulphuric and oxalic acids has been determined.

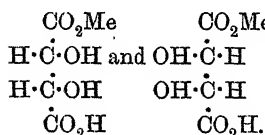
Manganous oxalate occurs as a pink trihydrate, which changes at the ordinary temperature to a colourless, stable dihydrate; the anhydrous salt is pink. The solubility of the dihydrate in water at 25° is 0.00218 gram-mol. per litre. In oxalic acid or ammonium oxalate the solubility is greater, probably owing to the formation of a mangano-oxalic acid,  $Mn(HC_2O_4)_2$ ; in accordance with this supposition, it is found that the solubility in sulphuric acid is greater than that in water, and is only slightly diminished by the addition of oxalic acid.

The most favourable condition for the separation of manganese from metals of the cerium group is the addition of a large excess of a concentrated solution of oxalic acid to a solution of the oxalates in an acid of 2.5 normality; the precipitate, however, even after a repetition of the process still contains manganese. C. S.

**Velocities of Addition of Bromine to Itaconic, Citraconic, and Mesoconic Acids. I.** ARNALDO PIUTTI and G. CALCAGNI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 18—22).—The authors have measured the velocities of addition of bromine to itaconic, citraconic, and mesaconic acids in aqueous solution at 25°. The addition takes place very rapidly in all three cases, and is complete for the maleic forms, citraconic (910 seconds) and itaconic (967 seconds) acids, after about equal times; for mesaconic acid, which is fumaroid in structure, 2715 seconds are taken. These results are in agreement with the observation of Bauer (Abstr., 1904, i, 841), Bauer and Moser (Abstr., 1907, i, 307), and Abati (this vol., i, 104), that with *cis*-forms the addition of bromine is far more rapid than with the corresponding *trans*-modifications. With citraconic and itaconic acids the constants of the reaction undergo very great variations, at first oscillating about a certain value, and then increasing more and more rapidly until the reaction is complete. With mesaconic acid, these variations are small, the constant increasing somewhat only towards the end of the reaction.

T. H. P.

**Optically Active Methyl Hydrogen Esters of the Tartaric Acids.** WILLY MARCKWALD and L. KARCZAG (*Ber.*, 1909, 42, 1518—1522).—In accordance with theory, it has been found possible to prepare from *i*-tartaric acid two optically active methyl hydrogen



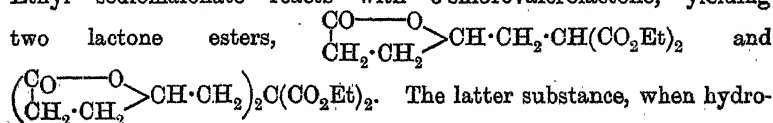
esters, which may be represented by the annexed formulæ. It is not yet known which formula belongs to which acid.

Methyl hydrogen *d*-tartrate crystallises with  $1\text{H}_2\text{O}$ , the presence of which has hitherto been overlooked (compare Walden, *Abstr.*, 1898, ii, 149). The optical rotatory power of the aqueous solution is  $[\alpha]_{\text{D}}^{25} + 14\cdot56^\circ (c=35)$ ,  $[\alpha]_{\text{D}}^{17\cdot5} + 16\cdot05^\circ (c=21)$ ,  $[\alpha]_{\text{D}}^{15\cdot5} + 18\cdot41^\circ (c=10\cdot5)$ ,  $[\alpha]_{\text{D}}^{13} + 18\cdot71^\circ (c=6\cdot3)$ ; the crystalline calcium salt,  $(\text{C}_5\text{H}_7\text{O}_6)_2\text{Ca}\cdot5\text{H}_2\text{O}$ ,  $[\alpha]_{\text{D}}^{20} + 17\cdot80^\circ (c=22\cdot5)$ ,  $+ 18\cdot56^\circ (c=10\cdot1)$ ,  $+ 17\cdot32^\circ (c=5\cdot06)$ , was also prepared.

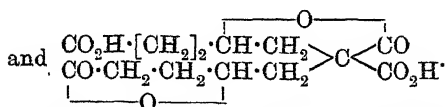
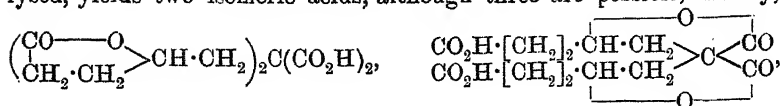
*i*-Tartaric acid, when boiled with an equal weight of methyl alcohol for six to seven hours, yields *r*-methyl hydrogen mesotartrate,  $\text{C}_5\text{H}_8\text{O}_6$ , a crystalline solid, m. p.  $82^\circ$ , and methyl mesotartrate,  $\text{C}_6\text{H}_{10}\text{O}_6$ , crystallising in glistening needles, m. p.  $111^\circ$  (compare Anschütz, *Abstr.*, 1888, 448). The calcium salt of the racemic hydrogen ester crystallises with  $3\text{H}_2\text{O}$ . The racemic compound is readily resolved through the strychnine salts. The strychnine salt of the levorotatory methyl hydrogen ester is soluble with difficulty in water, and has m. p.  $118$ — $119^\circ$ ; the more soluble strychnine salt of the dextrorotatory ester has m. p.  $97^\circ$ . The dextrorotatory ammonium salt of the methyl hydrogen ester,  $\text{C}_5\text{H}_7\text{O}_6\cdot\text{NH}_4$ , forms colourless crystals,  $[\alpha]_{\text{D}}^{21} + 13\cdot28^\circ (c=30)$ ,  $+ 17\cdot08^\circ (c=12)$ ,  $+ 18\cdot09^\circ (c=6)$ ; the corresponding calcium salt,  $(\text{C}_5\text{H}_7\text{O}_6)_2\text{Ca}\cdot4\text{H}_2\text{O}$ , forms white crystals,  $[\alpha]_{\text{D}} + 6\cdot7^\circ (c=6)$ , and when decomposed with oxalic acid yields levorotatory methyl hydrogen mesotartrate, obtained as a syrup,  $[\alpha]_{\text{D}}^{17} - 5\cdot43^\circ (c=9\cdot2)$ .

The levorotatory ammonium salt has  $[\alpha]_{\text{D}} - 20\cdot83^\circ (c=6)$ ; the corresponding calcium salt has  $[\alpha]_{\text{D}} - 7\cdot3^\circ (c=5)$ . W. H. G.

**Application of  $\delta$ -Chlorovalerolactone in the Preparation of Acids and Lactones.** HERMANN LEUCHS and ERNESTO MÖBIS (*Ber.*, 1909, 42, 1228—1238. Compare *Abstr.*, 1908, i, 510).— $\delta$ -Chlorovalerolactone may be employed with great advantage in the preparation of valerolactone and  $\delta$ -hydroxyvalerolactone; in the first case the chloro-compound is treated with phosphorus and hydriodic acid, whilst in the second it is acted on by alkalis.  $\delta$ -Chlorovalerolactone reacts with potassium cyanide in alcoholic solution, yielding  $\delta$ -cyanovalerolactone, which is, however, almost entirely converted by the action of more potassium cyanide into  $\delta$ -dicyanobutane- $\alpha$ -carboxylic acid. The latter substance when hydrolysed yields butane- $\alpha\beta\delta$ -tricarboxylic acid, this being the best method of obtaining this acid. Ethyl sodiomalonate reacts with  $\delta$ -chlorovalerolactone, yielding



lysed, yields two isomeric acids, although three are possible, namely,



*Ethyl αβ-dicyanobutane-δ-carboxylate*,  $\text{C}_9\text{H}_{12}\text{O}_2\text{N}_2$ , prepared by acting on an alcoholic solution of δ-chlorovalerolactone with potassium cyanide and treating the product so formed with an alcoholic solution of hydrogen chloride, is a colourless, viscid oil, b. p. 198–200°/14 mm. (corr.); the corresponding *acid* was obtained as a viscous, non-crystalline mass; the *sodium* salt,  $\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{Na}$ , forms small needles; the *silver* salt,  $\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{Ag}$ , was prepared and analysed; the *amide*,  $\text{C}_7\text{H}_9\text{ON}_2$ , crystallises in large, hexagonal plates, m. p. 90–91° (corr.).

δ-Cyanovalerolactone was not isolated from the product obtained by the interaction of δ-chlorovalerolactone and potassium cyanide, but its presence was demonstrated by conversion into *γ-hydroxyadipic acid*

*lactone*,  $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , microscopic crystals, m. p.

201–202° (corr.). The latter substance is converted by alcoholic hydrogen chloride and subsequent treatment with alcoholic ammonia

into *pyrrolidone-α-acetamide*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \diagup \quad \diagdown \\ \text{CO} \text{---} \text{NH} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , crystal-

lising in colourless needles and thin prisms, m. p. 149–150° (corr.).

The *lactone ester*,  $\text{C}_{12}\text{H}_{18}\text{O}_6$ , mentioned previously, is a heavy oil, b. p. 218–220°/14 mm.; the corresponding *acid* was obtained as a colourless syrup; the *silver* salt,  $\text{C}_8\text{H}_9\text{O}_7\text{Ag}_3$ , was prepared and analysed; the *amide*,  $\text{NH}_2 \cdot \text{CO} \cdot [\text{CH}_2]_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{CO} \cdot \text{NH}_2)_2$ , crystallises in needles and small prisms, m. p. 154–155° (decomp., corr.).

The *lactone ester*,  $\text{C}_{17}\text{H}_{24}\text{O}_8$ , crystallises in tufts of colourless needles, m. p. 122–123° (corr.); the *amide*,  $\text{C}_{13}\text{H}_{18}\text{O}_6\text{N}_2$ , crystallises in four-sided plates, m. p. 239–240° (corr.).

The ester when hydrolysed yields a mixture of two isomeric *acids*,  $\text{C}_{13}\text{H}_{16}\text{O}_8$ ; the one crystallises in colourless, iridescent, hexagonal leaflets or long needles, m. p. 235–236°, at which temperature it loses  $\text{CO}_2$ ; the other crystallises in colourless, broad prisms or four-sided plates, m. p. 180–181°, and loses carbon dioxide above this temperature.

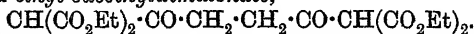
W. H. G.

**Dibasic Ketonic Acids. II. Ethyl α-Oxalylglutarate. α-Keto-adipic Acid.** HENRI GAULT (*Compt. rend.*, 1909, 148, 1113–1115. Compare Abstr., 1908, i, 713; this vol., i, 134).—Condensation of ethyl oxalate with ethyl glutarate is brought about by sodium ethoxide in ethereal solution with formation of a mixture of ethyl 4:5-diketocyclopentane-1:3-dicarboxylate (Dieckmann, Abstr., 1894, i, 324) and

*ethyl α-oxalylglutarate*,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{CO}_2\text{Et})\cdot\text{CO}_2\text{Et}_2$ . Under certain conditions, only the latter is obtained. The new ester loses carbon monoxide when distilled in a vacuum, and forms ethyl α-carboxyglutarate (Emery, Abstr., 1891, i, 54). On hydrolysis, it yields α-ketoadipic acid,  $\text{CO}_2\text{H}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ , m. p. 124°. W. O. W.

**Action of Chlorides of Dibasic Acids on Ethyl Sodiomalonate.** JOHANNES SCHEIBER (*Ber.*, 1909, 42, 1318—1323).—This work was undertaken with a view to the preparation of diketonic acids to be used in further syntheses.

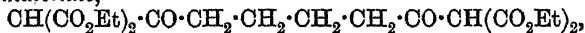
Succinyl chloride reacts with ethyl sodiomalonate to form a mixture of *ethyl 2:5-diketocyclopentane-1:1-dicarboxylate*,  $\begin{array}{c} \text{CH}_2\cdot\text{CO} \\ | \quad \diagup \\ \text{CH}_2\cdot\text{CO} \end{array} > \text{C}(\text{CO}_2\text{Et})_2$ , m. p. 68°, and *ethyl succinyl dimalonate*,



The former dissolves in most organic solvents, but not in water or aqueous alkalis, and gives no coloration with ferric chloride. It reacts with phenylhydrazine in acetic acid to form a *pyrazolone* derivative,  $\text{C}_{21}\text{H}_{20}\text{O}_3\text{N}_4$ , m. p. 177°, which is crystalline and gives an intense violet coloration with ferric chloride. Ethyl succinyl dimalonate was freed from the associated substance by treatment with a current of steam, and was then obtained as an oil. It dissolves unchanged in alkalis, gives a red coloration with ferric chloride, and yields a *dipyrzalone* derivative,  $\text{C}_{26}\text{H}_{26}\text{O}_6\text{N}_4$ , m. p. 188°, with phenylhydrazine in acetic acid.

Glutaric chloride reacts with ethyl sodiomalonate to form *ethyl glutaryl dimalonate*,  $\text{CH}(\text{CO}_2\text{Et})_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , which was obtained as a viscid oil. It gives a red coloration with ferric chloride, and with phenylhydrazine in acetic acid reacts to form a *dipyrzalone* derivative,  $\text{C}_{27}\text{H}_{28}\text{O}_6\text{N}_4$ , m. p. 118°, crystallising in pale yellow leaflets.

Adipic chloride condenses with ethyl sodiomalonate to give *ethyl adipyl dimalonate*,



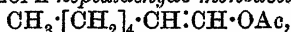
which was obtained as a viscous oil. It is hydrolysed readily by ammonia and by aniline, yielding respectively the amide and anilide of adipic acid. With phenylhydrazine in cold acetic acid it yields a *dipyrzalone* derivative,  $\text{C}_{28}\text{H}_{30}\text{O}_6\text{N}_4$ , m. p. 124°. T. A. H.

**Acetyl Sulphide.** EMIL FISCHER (*Ber.*, 1909, 42, 1070—1071).—*Acetyl sulphide*,  $\text{S}\cdot[\text{CH}_2\cdot\text{CH}(\text{OEt})_2]_2$ , is prepared by heating chloroacetal and potassium sulphide in concentrated aqueous-alcoholic solution in an autoclave at 130°. It is a colourless liquid, b. p. 143—147°/11 mm., or 280°/750 mm. (corr.; decomp.), easily soluble in organic solvents and distinctly so in water. E. F. A.

**Preparation of Acraldehyde.** GUSTAF FR. BERGH (*J. pr. Chem.*, 1909, [ii], 79, 351—357).—Five hundred grams of a mixture of 19 parts of glycerol, D 1.23, and one part of phosphoric acid, D 1.7, are placed in a metal still of 4 litres capacity, which is attached through a short condenser to a short-necked flask (750 c.c.) containing 100 grams

of sodium chloride immersed in a water-bath. The flask is attached through a long condenser to a receiver, consisting of an ordinary distilling bulb (300 c.c.) containing 15—20 grams of calcium chloride which has been treated with carbon dioxide. During the preparation, the water in the bath is kept boiling gently. The impurities are retained in the flask, and the acraldehyde which collects in the receiver is obtained pure by a single distillation. The yield is about 28%, the same as that obtained by Redtenbacher's potassium hydrogen sulphate method, but the author's process possesses the advantages that dehydrated materials need not be used, larger quantities can be employed, and the distillation can be commenced immediately after mixing. C. S.

**Constituents of Ethereal Oils.** *enol-n-Heptanal Acetate and enol-n-Octanal Acetate.* FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 1161—1163. Compare this vol., i, 239).—When *n*-heptaldehyde is boiled with acetic anhydride and sodium acetate, the products are unaltered aldehyde, *enol-n-heptaldehyde monoacetate*,



and the *diacetate*,  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OAc})_2$ . The yield of enolic acetate is about 50%. It is a colourless oil, b. p. 76—79°/10 mm.,  $D^{20}_D$  0.888,  $n_D$  1.43258. The diacetate has b. p. 122—124°/10 mm.,  $D^{20}_D$  0.963,  $n_D$  1.427. When boiled for some time under atmospheric pressure, it yields acetic acid and the aldehyde or its monoacetate.

*n-Heptaldehydesemicarbazone*,  $\text{C}_7\text{H}_{14} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , crystallises from methyl alcohol, and has m. p. 106—107°. *n-Octaldehyde* behaves in a similar manner with acetic anhydride and sodium acetate. *enol-n-Octaldehyde acetate*,  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} \cdot \text{CH} \cdot \text{OAc}$ , has b. p. 90—94°/10 mm.,  $D^{20}_D$  0.88, and  $n_D$  1.43256. The *diacetate* has b. p. 133—136°/10 mm.

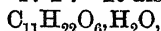
*n-Octaldehydeoxime*,  $\text{CH}_3 \cdot [\text{CH}_2]_6 \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$ , has b. p. 111—112°/9 mm. and m. p. 60°. The *semicarbazone*,  $\text{C}_8\text{H}_{16} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , has m. p. 101°. J. J. S.

**Semi-aldehyde of Succinic Acid.** (A Correction.) ERNST ALEFELD (*Ber.*, 1909, 42, 1426. Compare this vol., i, 132).—The m. p. of the *p*-nitrophenylhydrazone of the semi-aldehyde is erroneously given as 158°; this substance has m. p. 175°. J. V. E.

**Tautomerism of Aliphatic Ketones.** V. H. HANOU (*Ber.*, 1909, 42, 1052—1055).—When heated in sealed tubes at above 200° with acetic anhydride and fused sodium acetate, the simple aliphatic ketones are converted into tautomeric enolic forms, with the exception of acetone, which instead yields a condensation product, mesityl oxide. The enolic form of diethyl ketone was obtained in the form of the *acetate*,  $\text{CH}_3\text{Me} \cdot \text{C}(\text{OAc}) \cdot \text{CHMe}$ , a colourless liquid, b. p. 124—125°, which gives the ketonic form on hydrolysis with potassium hydroxide. The enolic *acetate* of dipropyl ketone is a colourless, pleasant smelling oil, b. p. 145—147°. The oximes of both these ketones are derivatives of the keto-forms. Mixed ketones, such as methyl ethyl ketone, methyl propyl ketone, or benzylideneacetone, could not be converted into enolic derivatives. E. F. A.

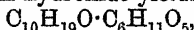
**Syntheses of Glucosides.** EMIL FISCHER and KARL RASKE (*Ber.*, 1909, 42, 1465—1476. Compare Abstr., 1894, i, 3; Königs and Knorr, *ibid.*, 1901, i, 369).—Glucosides have been obtained from *tert.*-amyl alcohol, menthol, and borneol by condensing  $\beta$ -acetobromoglucose (Moll van Charante, Abstr., 1902, i, 426) with the alcohols in presence of freshly precipitated silver carbonate.

*Tetra-acetyl- $\beta$ -amylglucoside*,  $C_5H_{11} \cdot O \cdot C_6H_7O_5Ac_4$ , crystallises from dilute alcohol in long, slender, glistening needles, m. p. 122—123° (corr.). When hydrolysed with cold barium hydroxide solution, it yields  *$\beta$ -amylglucoside*,  $C_5H_{11}O \cdot C_6H_{11}O_5$ , which crystallises from ethyl acetate in brilliant needles, m. p. 125—126° (corr.), after sintering at a lower temperature, and has  $[\alpha]_D^{20} - 17.2^\circ$ . It also forms a *hydrate*,



which crystallises from ether in needles, m. p. 113°.

*Tetra-acetylmenthyl-d-glucoside*,  $C_{10}H_{19} \cdot O \cdot C_6H_7O_5Ac_4$ , crystallises from 50% alcohol in long, colourless needles, m. p. 130° (corr.). It is fairly stable towards acid hydrolysing agents, but with an aqueous alcoholic solution of barium hydroxide yields *menthyl-d-glucoside*,



which crystallises from water in large, rectangular plates containing  $1H_2O$ , and melting at 77—79° (corr.). It has  $[\alpha]_D^{20} - 93.0^\circ$  in alcoholic solution. When heated at 100° under 15 mm. it loses its water of hydration. It is more readily hydrolysed than the amylglucoside by emulsin or acids.

*Tetra-acetylbornyl-d-glucoside*,  $C_{24}H_{36}O_{10}$ , crystallises from dilute alcohol in slender needles, m. p. 119—120° (corr.). *d-Bornyl-d-glucoside*,  $C_{16}H_{28}O_6$ , crystallises from water in large needles containing  $1H_2O$ , which it loses when heated over phosphoric oxide at 122°/15 mm. It has m. p. 134—136° and  $[\alpha]_D^{20} - 42.1^\circ$ , is fairly readily hydrolysed by acids, but only slowly by emulsin.

*Tetra-acetylglucovanillin*,  $C_8H_7O_2 \cdot O \cdot C_6H_7O_5Ac_4$ , obtained by shaking for three days an aqueous solution of the sodium derivative of vanillin with an ethereal solution of acetobromoglucose, crystallises from dilute alcohol in thin, glistening prisms, m. p. 143—144° (corr.), and when hydrolysed with barium hydroxide yields glucovanillin (Tiemann, Abstr., 1885, 980).

J. J. S.

**Phenylthiolglucosides.** EMIL FISCHER and KONRAD DELBRÜCK (*Ber.*, 1909, 42, 1476—1482).—Acetyl derivatives of phenylthiolglucosides have been prepared by shaking an ethereal solution of  $\beta$ -acetobromoglucose with an aqueous solution of the sodium derivative of a thiophenol for two days.

*Tetra-acetylphenylthiolglucoside*,  $SPh \cdot C_6H_7O_5Ac_4$ , crystallises from hot alcohol in small prisms, m. p. 118° (corr.), has  $[\alpha]_D^{20} - 40.1^\circ$ , is only sparingly soluble in water, and not readily hydrolysed by acids. *Phenylthiolglucoside*,  $SPh \cdot C_6H_{11}O_5$ , obtained by hydrolysing the acetyl derivative with barium hydroxide, crystallises from ethyl acetate in needles, m. p. 135° (corr.). It has  $[\alpha]_D^{20} - 72.5^\circ$ , is readily soluble in water, has a bitter taste, and is not hydrolysed readily by emulsin.

*Hepta-acetylphenylthiol-lactoside*,  $SPh \cdot C_{12}H_{14}O_{10}Ac_7$ , obtained from hepta-acetyl bromolactose (Ditmar, Abstr., 1902, i, 533) and sodium thio-

phenol, crystallises from alcohol in colourless prisms, m. p.  $167^{\circ}$  (corr.). It has  $[\alpha]_D^{20} - 17.7^{\circ}$ , and is only sparingly soluble in water. *Phenylthiol-lactoside*,  $\text{SPh} \cdot \text{C}_{12}\text{H}_{21}\text{O}_{10}$ , crystallises from hot alcohol in needles, m. p.  $221^{\circ}$  (corr.), has  $[\alpha]_D^{20} - 40.1^{\circ}$ , and is only sparingly soluble in water. When heated with *N*-sulphuric acid for one hour at  $100^{\circ}$ , it yields phenylthiolglucoside and galactose. It is also partly hydrolysed by emulsin, yielding phenylthiolglucoside. J. J. S.

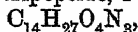
**Formation of Hydrocelluloses by means of Sulphuric Acid.** CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1909, 22, 929—931. Compare this vol., i, 136).—Attention is again drawn to the fact that elementary analyses are of little use in the examination of hydrocelluloses. If the molecular weight of cellulose is very large, it is impossible to determine by elementary analysis whether water has entered the molecule or not, unless the amount of water introduced is large (compare Franchimont, *Rec. trav. Chim.*, 1883, 2, 244; Büttner and Neumann, this vol., i, 86). J. J. S.

**Synthesis of Polypeptides. XXIX. Derivatives of *l*-Leucine, *d*-Alanine, and Glycine.** EMIL FISCHER and JOSEPH STEINGROEVEY (*Annalen*, 1909, 365, 167—180. Compare Abstr., 1908, i, 957).—The polypeptides glycyl-*l*-leucine, *l*-leucylglycyl-*d*-alanine, *l*-leucylglycyl-*l*-leucine, and *l*-leucyltriglycyl-*l*-leucine have been prepared in the usual manner. The first three were obtained in a crystalline state; the fourth, however, could not be crystallised. The first two substances were also obtained in an optically pure condition, since various preparations were found to have identical optical properties. This cannot be said of the other two compounds.

*Chloroacetyl-l-leucine*,  $\text{C}_8\text{H}_{14}\text{O}_3\text{NCl}$ , prepared from *l*-leucine and chloroacetyl chloride (compare Fischer and Warburg, Abstr., 1905, i, 690), crystallises in rectangular plates, m. p.  $136^{\circ}$  (corr.),  $[\alpha]_D^{20} - 14.4^{\circ}$  ( $\pm 0.2^{\circ}$ ) in alcohol. It is converted by ammonia into *glycyl-l-leucine*,  $\text{C}_5\text{H}_{16}\text{O}_3\text{N}_2$ , crystallising in small, long, thin plates, m. p.  $242^{\circ}$  (corr., decomp.),  $[\alpha]_D^{20} - 34.9^{\circ}$  ( $\pm 0.2^{\circ}$ ) in water. The latter substance yields *l*-leucylglycine anhydride identical with that prepared from *l*-leucylglycine (Abstr., 1906, i, 808).

*d*- $\alpha$ -*Bromoisohehexoylglycyl-d-alanine*,  $\text{C}_{11}\text{H}_{19}\text{O}_4\text{N}_2\text{Br}$ , prepared from *d*- $\alpha$ -bromoisohehexoylglycine (compare Abstr., 1905, i, 263) and *d*-alanine ethyl ester, forms colourless crystals, sinters at  $112.5^{\circ}$  (corr.), m. p.  $118^{\circ}$  (corr.),  $[\alpha]_D^{20} + 20.4^{\circ}$  ( $\pm 0.2^{\circ}$ ) in alcohol. It is converted by ammonia into *l*-leucylglycyl-*d*-alanine,  $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}_3$ , which forms tufts of slender needles, sinters at  $238^{\circ}$  (corr.), m. p.  $249^{\circ}$  (corr.),  $[\alpha]_D^{20} + 20.3^{\circ}$  ( $\pm 0.2^{\circ}$ ) in water.

*d*- $\alpha$ -*Bromoisohehexoylglycyl-l-leucine*,  $\text{C}_{14}\text{H}_{25}\text{O}_4\text{N}_2\text{Br}$ , prepared either by the interaction of *d*- $\alpha$ -bromoisohehexoylglycyl chloride and *l*-leucine ester or of *d*- $\alpha$ -bromoisohehexoyl chloride and glycyl-*l*-leucine, crystallises in microscopic prisms, m. p.  $100$ — $101^{\circ}$  (corr.),  $[\alpha]_D^{20} + 29.1^{\circ}$  ( $\pm 0.2^{\circ}$ ) in alcohol. The corresponding tripeptide, *l*-leucylglycyl-*l*-leucine,



is a colourless, crystalline powder; it is similar in m. p. and solubility to the racemic compound (compare Abstr., 1905, i, 863).

*d*- $\alpha$ -Bromoisohexoyltriglycyl-L-leucine,  $C_{18}H_{31}O_6N_4Br$ , prepared from *d*- $\alpha$ -bromoisohexoyldiglycylglycyl chloride (Abstr., 1907, i, 485) and L-leucine, crystallises in small, spherical aggregates of colourless needles, sinters at  $179^\circ$  (corr.), m. p.  $182^\circ$  (corr.),  $[\alpha]_D^{20} + 23.5^\circ (\pm 0.3^\circ)$  to  $+ 22.4^\circ (\pm 0.3^\circ)$  in water containing slightly more than the theoretical quantity of sodium hydroxide; the optical rotatory power of the solution when kept becomes gradually smaller. L-Leucyltriglycyl-L-leucine,  $C_{18}H_{33}O_6N_5$ , prepared from the substance just described, is obtained as a somewhat hygroscopic, amorphous, white powder, which becomes yellow at  $213^\circ$  (corr.), then sinters, and finally decomposes at  $229^\circ$  (corr.),  $[\alpha]_D^{20} + 21.1^\circ (\pm 0.8^\circ)$  to  $+ 21.3^\circ (\pm 0.4^\circ)$  in water.

W. H. G.

**Synthesis of Polypeptides. XXX. Derivatives of l-Cystine.** EMIL FISCHER and OTTO GERNGROSS (*Ber.*, 1909, 42, 1485—1495).—Symmetrical tripeptides containing cystine were prepared from inactive  $\alpha$ -halogen fatty acids by Fischer and Suzuki (Abstr., 1905, i, 30), and were probably mixtures of stereoisomerides. A crystalline *di*-L-leucyl-L-cystine is now obtained from *d*- $\alpha$ -bromoisohexoic acid. This, like the synthetic leucyltriglycyltyrosine, is precipitated by ammonium sulphate even from dilute aqueous solution, and may be termed an albumose.

L-Cystine when coupled with halogenacyl chlorides in alkaline solution forms monohalogenacyl as well as dihalogenacyl derivatives. The former are converted by ammonia into the corresponding dipeptides.

*Di*-*d*- $\alpha$ -bromoisohexoyl-L-cystine forms pointed, hard prisms in stellar aggregates, m. p.  $121$ — $123^\circ$  (corr.), and has  $[\alpha]_D^{20} - 133^\circ$ . *Di*-L-leucyl-L-cystine,  $S_2[CH_2 \cdot CH(CO_2H) \cdot NH \cdot CO \cdot CH(NH_2) \cdot C_4H_9]_2$ , is obtained as a granular product, which turns yellow at  $200^\circ$  and decomposes at higher temperatures; it has  $[\alpha]_D^{20} - 136.6^\circ$ . It is also obtained after some trouble in minute, well-formed prisms or needles, which have a slightly higher rotatory power,  $[\alpha]_D^{20} - 141.4^\circ$ ; it gives a reddish-violet coloration with copper sulphate. Especially characteristic is the precipitation by ammonium sulphate.

*Mono*-*d*- $\alpha$ -bromoisohexoyl-L-cystine,

$C_4H_9 \cdot CHBr \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot CH(CO_2H) \cdot NH_2$ , obtained on coupling *d*- $\alpha$ -bromoisohexoyl chloride with excess of cystine, has m. p.  $194^\circ$  (decomp.),  $[\alpha]_D^{21} - 130.2^\circ$ ; it crystallises in colourless plates or needles. When treated with aqueous ammonia it forms L-leucyl-L-cystine, which, when heated, darkens at  $165^\circ$ , but could not be obtained quite pure.

*Chloroacetyl*-L-cystine, prepared by the interaction of chloroacetyl chloride with excess of cystine, crystallises in colourless, rectangular prisms or plates, decomp.  $185$ — $190^\circ$ , and has  $[\alpha]_D^{17} - 169^\circ$ . *Glycyl*-L-cystine was obtained by warming the foregoing with 25% aqueous ammonia at  $70^\circ$ , but could not be completely purified. *Di*(chloroacetyl)-L-cystine crystallises from water +  $1H_2O$  in needles, which sinter at  $90^\circ$ . In alcohol the anhydrous substance has  $[\alpha]_D^{20} - 120.3^\circ$ . E. F. A.

**Preparation of Glycocyamines or Guanino-acids. II.** HENRIK RAMSAY (*Ber.*, 1909, 42, 1137—1140. Compare this vol., i, 88).—L- $\alpha$ -Bromopropionic and *d*- and L- $\alpha$ -bromoisohexoic acids have

been converted by a concentrated aqueous solution of guanidine into the corresponding guanino-acids by the method described previously. Despite the fact that a lower temperature,  $20^{\circ}$ , is maintained, the  $\alpha$ -guaninopropionic acid is almost completely racemised; somewhat better results are obtained with the other two active acids,  $l$ - $\alpha$ -guaninoisohexoic acid and the  $d$ -isomeride having  $[\alpha]_D^{20}$   $4.54^{\circ}$  and  $-4.08^{\circ}$  respectively in hydrochloric acid. By warming  $l$ - $\alpha$ -guaninoisohexoic acid with barium hydroxide,  $l$ -leucine is obtained. Since  $l$ - $\alpha$ -bromoisohexoic acid and ammonium hydroxide yield  $d$ -leucine, Walden's inversion must have occurred at some stage in the preceding reactions. C. S.

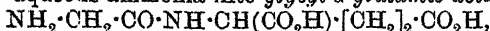
**Derivatives of Glutamic Acid.** EMIL FISCHER, WALTER KROPP, and ALEX STAHLSCHMIDT (*Annalen*, 1909, 365, 181—200).—The study of the polypeptides of glutamic acid is of the greatest importance, since glutamic acid is present in many vegetable proteins; however, owing to experimental difficulties, only one dipeptide, namely,  $l$ -leucyl- $d$ -glutamic acid, has been described hitherto (Abstr., 1907, i, 901). The present communication treats of the preparation and properties of further polypeptides of glutamic acid. Since the compounds obtained from pure chloroacetyl- $d$ -glutamic acid were but slightly optically active, possibly because racemisation had occurred during the processes of preparation, experiments were performed with  $dl$ -glutamic acid in the hope that better yields would be obtained, but this was not the case.

$dl$ -Glutamic acid, prepared by the method of Schulze and Bosshard (Abstr., 1886, 373), crystallises from water at  $37^{\circ}$  in needles belonging to the rhombic system; m. p.  $199^{\circ}$  (corr.), when heated quickly. Measurements of the crystals are given in the original.

*Chloroacetyl-d-glutamic acid,*

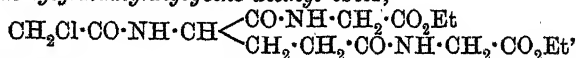


prepared by the action of chloroacetyl chloride on  $d$ -glutamic acid in the presence of sodium hydroxide at  $0^{\circ}$ , crystallises in slender prisms or needles, m. p.  $143^{\circ}$  (corr.),  $[\alpha]_D^{20} -13.5^{\circ}$  ( $\pm 0.2^{\circ}$ ) in water. It is converted by aqueous ammonia into *glycyl-d-glutamic acid*,

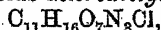


an amorphous, white powder, which sinters at about  $165^{\circ}$ , m. p.  $178^{\circ}$  (corr.),  $[\alpha]_D^{20} -6.3^{\circ}$  in water; the copper salt,  $\text{C}_7\text{H}_{10}\text{O}_5\text{N}_2\text{Cu}_3\frac{1}{2}\text{H}_2\text{O}$ , is a pale blue, granular powder; the anhydrous salt decomposes at  $213^{\circ}$  (corr.).

*Chloroacetylglutamylglycine diethyl ester,*



is prepared by the action of phosphorus pentachloride on chloroacetylglutamic acid suspended in acetyl chloride, and subsequent treatment of the acid chloride so formed with glycine ethyl ester; it crystallises in spherical aggregates of small, slender needles, sinters at  $140^{\circ}$ , m. p.  $146^{\circ}$  (corr.), and when treated with  $N$ -sodium hydroxide solution and then sulphuric acid, yields *chloroacetylglutamylglycine*,



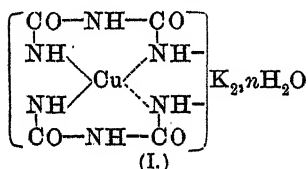
crystallising in spherical aggregates of slender needles, m. p.  $173^{\circ}$  (decomp., corr.). The latter substance is converted by aqueous ammonia

into *glycylglutamyl diglycine*,  $C_{11}H_{15}O_7N_4$ , crystallising in slender needles, which become coloured at about  $220^\circ$  and decompose at  $248^\circ$  (corr.).

The following substances were prepared by the methods employed in the preparation of the active compounds just described.

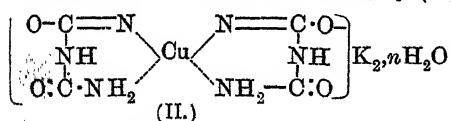
*Chloroacetyl-dl-glutamic acid* crystallises in microscopic needles and small, long leaflets, sinters at  $120^\circ$ , m. p.  $123^\circ$ . *Glycyl-dl-glutamic acid* is a hygroscopic, amorphous powder; the copper salt ( $3\frac{1}{2}H_2O$ ) crystallises in microscopic prisms and plates, and decomposes, when heated rapidly, at  $223^\circ$  (corr.). *Chloroacetylglutamyl diglycine diethyl ester* and *chloroacetylglutamyl diglycine*, prepared from chloroacetyl-dl-glutamic acid, are almost identical in physical properties with the corresponding compounds derived from chloroacetyl-d-glutamic acid; naturally, they are optically quite inactive. W. H. G.

**Complex Compounds. II. Compounds Showing the Biuret Reaction.** LEO A. TSCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 166—184. Compare Abstr., 1907, i, 595).—The author discusses the



structure both of compounds giving the biuret reaction and of the compounds formed by this reaction. He is of opinion that the compounds formed have a cyclic structure; that of the compound obtained when a copper salt, potassium hydroxide, and biuret are used being expressed by (I), or assuming that the

biuret acts in its tautomeric form, by (II).



Similar formulæ are given for the corresponding compounds yielded by dicyanodiamidine and diguanide.

The preparation and properties are described

of the alkali metal salts of succinimide having the composition  $[Cu(C_4H_4O_2N)_4]M_2, nH_2O$  (*loc. cit.*).

The work of Ley and Krafft (Abstr., 1907, i, 301), and Ley and Müller (Abstr., 1907, i, 730), is discussed. T. H. P.

**Fulminic Acid. III. Polymerisation of Fulminic Acid.** HEINRICH WIELAND and HERMANN HESS (*Ber.*, 1909, 42, 1346—1363).

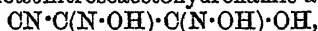
—The work of Ehrenberg (Abstr., 1884, 419; 1885, 1192), Scholvien (*ibid.*, 1885, 39; 1886, 137), and Nef (*ibid.*, 1895, i, 9) on fulminic acid and its derivatives is discussed, and from new experimental data it is shown (a) that fulminic acid can exist in the free state in solution in ether as stated by Scholvien; (b) that metafulminuric acid (isocyanuric acid) is the sole product of its spontaneous polymerisation, and

(c) that the formula  $N \begin{smallmatrix} \text{CH}\cdot\text{C}\cdot\text{N}\cdot\text{OH} \\ \diagup \quad \diagdown \\ \text{O}-\text{C}\cdot\text{N}\cdot\text{OH} \end{smallmatrix}$  accounts better for the reactions of metafulminuric acid, and particularly for its conversion by ammonia and alkalis into cyanoisnitrosoacetohydroxamic acid (see below), than that proposed by Nef.

Cold dilute sulphuric acid was added to an aqueous solution of sodium fulminate until the latter was just acid to Congo-red paper, and the

liberated fulminic acid was extracted by ether. This solution was then shaken with silver nitrate solution, and slightly acidified with nitric acid, when silver fulminate crystallised out and the aqueous mother liquor was found to contain no sulphuric acid. There is therefore no evidence in favour of Nef's view, that, under the conditions described, free fulminic acid is not formed and dissolved out by the ether, but only an additive compound of this with sulphuric acid. It was also found that on allowing an ethereal solution of fulminic acid to distil under reduced pressure, some fulminic acid was carried over with the ether vapour, and could be absorbed by cooled silver nitrate solution, yielding silver fulminate.

Metafulminuric acid (isocyanuric acid), m. p. 85—86° (hydrated), 106° (anhydrous), is best obtained by the action of small quantities of sodium hydroxide on chloroformoxime (Nef, *Abstr.*, 1895, i, 10). It probably contains  $1\text{H}_2\text{O}$ , not  $3\text{H}_2\text{O}$ , as stated by Scholvien (*loc. cit.*: compare Palazzo and Tamburello, *Abstr.*, 1907, i, 298). The colour reactions given by the acid with various metallic salts in solution are detailed in the original. The acid is also formed as a first product when ammonia solution reacts in the cold with chloroformoxime, but on warming with ammonia, or by the further action of alkalis on metafulminuric acid, cyanoisonitrosoacetohydroxamic acid,



m. p. 117—118° (Nef, *loc. cit.*), is formed. Scholvien's secondary yellow ammonium salt (*loc. cit.*) is probably ammonium cyano-oximinoacetohydroxamate.

When hydroxylamine reacts with chloroformoxime, or, better, with cyano-oximinoacetohydroxamic acid, the amino-oxime of oximinomalonohydroxamic acid,  $\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{OH}$ , is formed, and is best isolated in the form of its well-crystallised hydrochloride, m. p. 151—152° (decomp.). The latter gives characteristic reactions with aqueous solutions of a number of metallic salts, liberates iodine from potassium iodide solution, but does not reduce Fehling's solution. The amino-oxime could not be obtained pure; it yields a crystalline barium salt and a tetra-acetyl derivative, m. p. 177° (decomp.), which is crystalline and difficultly soluble. When heated in aqueous acid or alkaline solution, the amino-oxime is converted

into amino-oximinoisooxazolone,  $\text{NH}_2\cdot\text{C}\begin{matrix} \nearrow \text{C}(\text{N}\cdot\text{OH})\cdot\text{CO} \\ \searrow \text{N} \quad \text{O} \end{matrix}$ , m. p. 159°

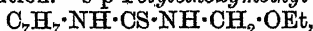
(decomp.), which crystallises from hot water in dull orange-yellow needles. It liberates iodine from potassium iodide solutions, slowly decolorises permanganate, dissolves in sulphuric acid with a yellow coloration, in hydrochloric acid with the formation of hydroxylamine, and in dilute nitric acid with the liberation of hydrocyanic acid. Alkalis convert it into salts of the amino-oxime of oximinomalononic acid,  $\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. 166° (decomp.), which is best isolated as the barium salt. The acid crystallises from hot water in clusters of colourless needles, is readily soluble in pyridine, and only slightly so in alcohol, ether, or acetic acid. It gives characteristic colorations with aqueous solutions of various metallic salts.

T. A. H.

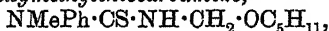
**Thiocyanates and Thiocarbimides. VIII. New Class of Thiocarbimides.** Thiocarbimido-ethers. TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1909, 41, 337—344. Compare Abstr., 1907, i, 910).—Previous work has shown that the interaction of potassium thiocyanate and primary alkyl halides of the type  $R \cdot CH_2X$ , where R is any saturated or unsaturated organic radicle, leads generally to the formation of thiocyanates; only when R is vinyl or a derivative of vinyl are thiocyanates obtained, which are readily changed to thiocarbimides by heating. Now it is found that chloromethyl ether, chloromethyl ethyl ether, and chloromethyl isoamyl ether react almost quantitatively with potassium thiocyanate to form the corresponding thiocarbimides, the structure of which is proved by desulphurising them by warm alkaline lead acetate, by the formation of carbon disulphide by thiobenzoic acid, and by their combination with ammonia or amines to form a new class of thiocarbimides,  $NHR' \cdot CS \cdot NH \cdot CH_2 \cdot OR$ ; the oxygen analogue of the parent substance of this class, monomethylolcarbamide, has been obtained by Einhorn and Hamburger (Abstr., 1908, i, 141). These results are not in harmony with Michael's theory that a strongly negative character of the halide favours the production of thiocarbimides.

*isoThiocyanodimethyl ether* [*thiocarbimidodimethyl ether*],  
 $OMe \cdot CH_2 \cdot NCS$ ,

b. p.  $138^\circ/770$  mm., and  $56-60^\circ/30$  mm., obtained by digesting a solution of chlorodimethyl ether in benzene with potassium thiocyanate for two days at  $110^\circ$ , is a colourless oil with an irritating odour. *Thiocarbimidomethyl ethyl ether*,  $OEt \cdot CH_2 \cdot NCS$ , b. p.  $93-97^\circ/97-100$  mm., and *thiocarbimidomethyl isoamyl ether*,  $C_5H_{11} \cdot O \cdot CH_2 \cdot NCS$ , b. p.  $208^\circ-210^\circ/760$  mm. and  $122-125^\circ/34$  mm., possess similar properties. *Ethoxy-methylthiocarbamide*,  $OEt \cdot CH_2 \cdot NH \cdot CS \cdot NH_2$ , obtained from thiocarbimidomethyl ethyl ether and strong aqueous ammonia, has m. p.  $92-93^\circ$ . *s-Phenylethoxymethylthiocarbamide*,  $NHPh \cdot CS \cdot NH \cdot CH_2 \cdot OEt$ , m. p.  $125-126^\circ$ , is obtained from aniline and thiocarbimidomethyl ethyl ether in ethereal solution. *s-p-Tolylethoxymethyl thiocarbamide*,



m. p.  $120^\circ$ , is decomposed by concentrated ammonium hydroxide at  $140-150^\circ$ , *p*-toluidine being formed. *s-Phenylisoamylloxymethylthiocarbamide*,  $NHPh \cdot CS \cdot NH \cdot CH_2 \cdot O \cdot C_5H_{11}$ , and the corresponding *p-tolyl* compound have m. p.  $109^\circ$  and  $119^\circ$  respectively, whilst *phenylmethoxyisoamylloxymethylthiocarbamide*,



has m. p.  $87^\circ$ .

C. S.

**Organic Mercury Compounds.** EINAR BILLMANN and JOHANNES WITT (*Ber.*, 1909, 42, 1067—1070. Compare this vol., i, 17; Schrauth and Schoeller, Abstr., 1908, i, 617).—Polemical. Schrauth and Schoeller have described the formation of hydroxymercuriacetic anhydride by the interaction of sodium hydroxide, malonic acid, and mercuric oxide, whereby carbon dioxide is eliminated. In reality carbon dioxide is not eliminated, and a mercurimalonic acid, previously described by

Billmann (Abstr., 1902, i, 665), is formed and not a derivative of acetic acid. E. F. A.

**The Study of Hydro-aromatic Substances.** EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1908, 221—230).—This report contains a reply to Harries and Antoni's criticisms (Abstr., 1903, i, 613) on the work of Crossley and Le Sueur (*Trans.*, 1902, 81, 821), and an account of recent work on hydro-aromatic substances. T. H. P.

[1-Acetyl- $\Delta^1$ -cyclopentene as an Oxidation Product of  $\Delta^1$ -cyclo-Hexeneacetic Acid.] LOUIS BOUVEAULT (*Ber.*, 1909, 42, 1055—1057).—Some remarks on a paper by Perkin and Wallach (this vol., i, 154). The formation of cyclopentene from a derivative of cyclohexene is described as unexpected by Perkin and Wallach. It is pointed out that the reverse change is exemplified by the conversion of isolauronic acid into isolauronic acid at 0°, as well as by the conversion of  $\beta$ -campholenic acid into the isophorone of camphor. Confidence is to be placed in the oxidation with permanganate for the determination of constitution in the case of hydrocarbons of the methylcyclohexene type, but not in the case of cyclic, unsaturated hydrocarbons, which contain negative groups in the neighbourhood of the double bond. E. F. A.

**Action of Nitric Acid on Saturated Hydrocarbons. III.** S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 145—157. Compare this vol., i, 93).—The partial decomposition of the isonitro-compound, formed as an intermediate product in the action of nitric acid on saturated hydrocarbons, into aldehyde or ketone is accompanied by the evolution of nitrous oxide:  $2\text{CHR}\cdot\text{NO}\cdot\text{OH} = 2\text{R}\cdot\text{CHO} + \text{N}_2\text{O} + \text{H}_2\text{O}$ , and  $2\text{CR}_2\cdot\text{NO}\cdot\text{OH} = 2\text{R}_2\text{CO} + \text{N}_2\text{O} + \text{H}_2\text{O}$ .

In the action of nitric acid on cyclohexane, the cyclohexanone formed as above is oxidised quantitatively to adipic acid, but the proportion of nitrous oxide formed is about double that indicated by the above equation. The conclusion is drawn that the oxidation of the second methylene group to carboxyl proceeds in the same manner as that of the first group, giving rise in the first stage to  $\text{:C}\cdot\text{NO}\cdot\text{OH}$ , which is converted first into carbonyl, with evolution of nitrous oxide, and ultimately into carboxyl, with breaking of the ring.

The acids formed in the above reaction consist of adipic (80%), glutaric (13%), and succinic (7%) acids.

When cyclohexanone is treated with nitric acid, the proportion of nitrous oxide obtained is in agreement with the above views of the reaction. T. H. P.

**Influence of the Solvent on the Ratio of Isomerides [in Substitution].** LUDWIK BRUNER and J. VORBRÖDT (*Bull. Acad. Sci. Cracow*, 1909, 221—238. Compare Abstr., 1908, i, 146).—The bromination of alkylbenzenes in various solvents in the dark at 25° has been quantitatively studied, and the yields of the various isomerides measured. The  $\omega$ -bromo-derivatives are estimated, after

washing with ammonium nitrate, by precipitation with silver nitrate and titration of the excess with thiocyanate. When carbon disulphide is the solvent, this must be removed by evaporation before precipitating.

The hydrocarbons employed were toluene, ethylbenzene, the three xylenes, propylbenzene, and *sec*-butylbenzene, and the solvents carbon disulphide, carbon tetrachloride, benzene, chloroform, glacial acetic acid, nitrobenzene, and benzonitrile.

The ratio of chain-substituted to ring-substituted product is influenced by the solvent, ionising solvents favouring substitution in the nucleus. The order of the solvents is as given above, carbon disulphide being the least ionising, and therefore giving the highest yield of  $\omega$ -derivative. Thus with toluene, benzyl bromide forms 85% of the product in carbon disulphide, and only 4% in acetic acid and 2% in nitrobenzene. Since traces of moisture greatly affect the conductivity of nitrobenzene, the latter was tried in presence of phosphoric oxide, without alteration in the yield. With ethylbenzene in carbon tetrachloride or benzene, the reaction at 25° is so rapid that irregular results are obtained. The reaction is more uniform at 10°. With propylbenzene in carbon tetrachloride, the reaction is more rapid in dilute than in concentrated solutions, probably owing to the formation of complex acids from the hydrogen bromide and bromine, so reducing the effective concentration of the latter.

Similar influences prevail in the presence of light. Thus, the bromination of tetra- and penta-methylbenzene has been described as unaffected by light (Korczyński, *Abstr.*, 1902, i, 274), glacial acetic acid being used as the solvent. In carbon disulphide solution, however, the reaction is sensitive to light.

In the side-chain, the methylene group is the most readily substituted, the more so the longer the chain. Meta-substitution very greatly increases the tendency to brominate in the nucleus, the velocity constant for *m*-xylene being about one hundred times as great as those of *o*- and *p*-xylene.

C. H. D.

**Certain Reactions of Nitro-derivatives.** LIVIO CAMBI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 301—305).—From measurements of dispersion and refraction of alkyl nitrates, Brühl (*Abstr.*, 1898, ii, 362) drew the conclusion that these nitrates and nitric acid have a peroxide structure containing the group  $O \cdot O \cdot N \cdot O$ . Results tending to confirm this formula have been obtained by several authors (compare Klason and Carlson, *Abstr.*, 1906, i, 787; 1907, i, 1000; Carlson, *Abstr.*, 1907, i, 1001; Gutmann, *Abstr.*, 1908, i, 597). The author's work, however, is in direct disagreement with these results.

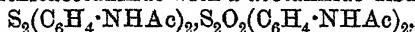
The fact that alkyl nitrates, in presence of alkali, oxidise thiophenol to phenyl disulphide, arsenites to arsenates, and alkali hydrosulphides to polysulphides, with formation of alkali nitrite, is explained by the above-named authors as due to the hydrolysis of the alkyl nitrates by the alkali proceeding in two different ways, yielding (1) alcohol and alkali nitrate, (2) aldehyde and alkali nitrite. The following oxidation processes, effected by aromatic nitro-derivatives, are, however, quite analogous to the above oxidations brought about by the alkyl nitrates:

(1) preparation of azoxy-derivatives by the action of alkoxides on aromatic nitro-derivatives; (2) reduction of nitro-derivatives to azoxy-compounds by means of alkali arsenites (Loesner, Abstr., 1895, i, 214); (3) interaction of potassium phenyl mercaptan and *m*-nitrobenzoate, yielding *m*-azoxybenzoic acid and phenyl disulphide. In these reactions, it may be assumed that the nitro-derivatives are reduced first to nitroso-derivatives, and the analogy between the reactions of the nitro-derivatives and those of the alkyl nitrates is clearly brought out in the case of, say, thiophenol:  $\text{CH}_2\text{R}\cdot\text{O}\cdot\text{NO}_2 + 2\text{Ph}\cdot\text{SK} + \text{H}_2\text{O} = \text{KO}\cdot\text{NO} + \text{Ph}_2\text{S}_2 + \text{KHO} + \text{CH}_2\text{R}\cdot\text{OH}$  and  $\text{R}\cdot\text{NO}_2 + 2\text{Ph}\cdot\text{SK} + \text{H}_2\text{O} = \text{R}\cdot\text{NO} + \text{Ph}_2\text{S}_2 + 2\text{KHO}$ .

This analogy of behaviour between the  $\text{NO}_2$  group in the nitro-derivatives and that in the alkyl nitrates indicates the identity of structure of the two groups, this view being supported by the fact that nitro-derivatives can be obtained by nitration by means of alkyl nitrates in presence of alkoxides:  $\text{:CH}_2 + \text{R}\cdot\text{O}\cdot\text{NO}_2 = \text{:CH}\cdot\text{NO}_2 + \text{R}\cdot\text{OH}$ .

Other evidence against the peroxide formula for the alkyl nitrates is also adduced (compare Baeyer and Villiger, Abstr., 1901, i, 308, 309; Carlson, *loc. cit.*).  
T. H. P.

$\alpha$ - and  $\beta$ -Acetanilide Disulphoxide. OSCAR HINSBERG (*Ber.*, 1909, 42, 1278—1284. Compare this vol., i, 6).—When 4:4'-dithioacetanilide [*p*-acetylaminophenyl disulphide] is left in contact with 3% hydrogen peroxide for some weeks at 25—30°, it is converted into a substance of the formula  $\text{C}_{22}\text{H}_{32}\text{O}_6\text{N}_4\text{S}_4$ , which appears to be a compound of  $\alpha$ -dithioacetanilide with  $\alpha$ -acetanilide disulphoxide,



since it decomposes into these two substances on boiling for one to two minutes with glacial acetic acid; when boiled with glacial acetic acid for half an hour, it yields an isomeric  $\beta$ -disulphoxide; the double compound when heated above its melting point is converted into  $\alpha$ -,  $\gamma$ -, and probably  $\beta$ -dithioacetanilide.

$\alpha$ -Acetanilide disulphoxide,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}\cdot\text{SO}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , crystallises from glacial acetic acid with  $2\text{C}_2\text{H}_4\text{O}_2$  in yellow plates, m. p. 190° (decomp.); prolonged washing with warm water converts it into a yellow, crystalline powder, which is free from acetic acid, but dissolves in alcohol to a colourless solution.

$\beta$ -Acetanilide disulphoxide crystallises from its colourless solution in alcohol in the form of yellowish-red rhombohedra, m. p. 233° (decomp.); it crystallises from glacial acetic acid in colourless needles, which contain two molecules of the solvent.

The fact that both these coloured substances give colourless solutions in alcohol is explained by assuming that the alcohol combines with them to form colourless additive compounds of the formula:  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{S}(\text{OH})(\text{OEt})\cdot\text{S}(\text{OH})(\text{OEt})\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ .  
P. H.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Report*, 1908, 115—118).—This report deals [with W. W. REED] with

the transformation of the crystalline 2:4-dichloroamino-1-nitroaminobenzene into 2:4-dichloro-6-nitroaniline, with the transformation of the nitroamine in solution, and with preliminary experiments on the molecular rearrangement of the unsubstituted nitroaminobenzene; and [with C. PEARSON] with the wandering of bromine in the transformation of nitroaminobromobenzenes.

T. H. P.

**Amino-hydroxydiphenylamine.** FRITZ ULLMANN and KARL JÜNGEL (*Ber.*, 1909, 42, 1077—1083. Compare *Abstr.*, 1908, i, 298, 975).—Nitro- and amino-hydroxydiphenylamines can be easily obtained by the method described by Ullmann and Dahmen (*Abstr.*, 1908, i, 975), which consists in condensing *p*-chloronitrobenzene-*o*-sulphonic acid with aniline, and the elimination, by heating with dilute mineral acids, of the sulphonyl group from the *p*-nitrodiphenylaminesulphonic acid formed, etc.

4-Nitro-4'-hydroxydiphenylamine-2-sulphonic acid forms a *potassium* salt,  $C_{12}H_9O_6N_2SK$ , crystallising in red needles, and a *barium* salt, crystallising in orange-yellow needles. The corresponding 4-amino-4'-hydroxydiphenylamine-2-sulphonic acid, formed on reduction of the nitro-compound, crystallises in needles, which give a reddish-brown and, finally, violet coloration with ferric chloride.

4-Nitro-4'-hydroxydiphenylamine forms lustrous, reddish-brown plates, *m. p.* 183°.

4-Nitro-4'-methoxydiphenylamine, prepared by alkylation with methyl sulphate, crystallises in steel-blue needles, *m. p.* 151°. The *p*-toluene-sulphonic ester of 4-nitro-4'-hydroxydiphenylamine forms yellow needles, *m. p.* 143°.

4-Amino-4'-hydroxydiphenylamine is prepared either by reduction of the nitro-compound or by the action of mineral acids on the amino-hydroxydiphenylaminesulphonic acid. It separates in large, almost colourless plates, *m. p.* 166°. The colourless solution in alkalis becomes a rich blue after a time, owing to formation of indamine; the solution in dilute hydrogen chloride is coloured an intense blue by ferric chloride. The *diacetate* separates in colourless, glistening plates, *m. p.* 141°.

4-Nitro-4'-methoxydiphenylamine-2-sulphonic acid, from chloronitrobenzenesulphonic acid and *p*-anisidine, forms a *potassium* salt, crystallising in yellow needles. The corresponding amino-compound forms almost colourless needles. By the action of mineral acids on the nitro-compound, 4-nitro-4'-methoxydiphenylamine is obtained. 4-Amino-4'-methoxydiphenylamine has *m. p.* 102°, and is identical with the product obtained by Jacobson and Jaenicke (*Abstr.*, 1897, i, 143) from benzeneazoanisole. Condensation with *o*-anisidine yields 4-nitro-2'-methoxydiphenylamine-2-sulphonic acid, of which the *potassium* salt forms yellow needles. The corresponding 4-amino-derivative, obtained on reduction, crystallises in colourless needles, which become faintly blue on exposure to air.

4-Nitro-2'-methoxydiphenylamine forms yellow needles with a steel-blue reflex, *m. p.* 111°; 4-amino-2'-methoxydiphenylamine separates in faintly rose-coloured needles, *m. p.* 80°.

E. F. A.

**Attempts to Prepare Isomeric Asymmetric Ammonium Compounds.** EMIL FRÖHLICH (*Ber.*, 1909, 42, 1561—1565).—An

nitric acid (D 1.4—1.52) it yields 2:3-dinitro-4-methylaminophenyl benzoate,  $\text{NHMe} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{OBz}$ , which crystallises in brownish-yellow needles, m. p. 178°. Nitration by a mixture of concentrated sulphuric acid and nitric acid leads to the formation of nitrobenzoyl-2:3-(or 2:6)dinitro-4-methylaminophenol, crystallising in lemon-yellow needles, m. p. 203—204°. W. H. G.

**So-called Photoanethole.** A Contribution to the Chemical Action of Light. PAUL HOERING and KARL PAUL GRÄLERT (*Ber.*, 1909, 42, 1204—1207).—The substance described by de Varda as photoanethole (Abstr., 1891, 1347) is shown to be 4:4'-dimethoxystilbene (compare Wiechell, Abstr., 1894, i, 507). It is probably formed by the action of sunlight on the anisaldehyde present in anethole which has been exposed to the action of the air and light.

4:4'-Dimethoxystilbene dibromide,  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Br}_2$ , crystallises in short needles, m. p. 178° (decomp.). W. H. G.

**Mechanism of the Resorcinol-Tartaric Colour Reaction.** GEORGES DENIGÈS (*Bull. Soc. chim.*, 1909, [iv], 5, 323—326).—In a previous paper (this vol., ii, 190) it has been shown that the red or reddish-violet colour given by certain substances in presence of sulphuric acid and resorcinol is associated with the presence in these substances of the group  $\text{HO} \cdot \text{C} \begin{smallmatrix} | \\ \text{C} \\ | \end{smallmatrix} \cdot \text{OH}$ , or a derivative of this. It is now found that the mechanism of the reaction consists in the formation of aldehydes from these substances, by the action of sulphuric acid and the condensation of these aldehydes with the resorcinol or other phenol used.

The nature of the aldehyde (or aldehydes) formed in a number of cases is discussed. Confirmation of this view is found in the fact that some substances, such as glycerol, which do not give a coloration when the test is applied in the usual manner (*loc. cit.*, and Abstr., 1896, ii, 80), give it after oxidation with permanganate. T. A. H.

**Reversible Substitution of Alkoxy Groups in the Benzene Ring.** JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 313—320. Compare this vol., i, 150).—When attached to the benzene nucleus and under the influence of *o*- or *p*-nitro-groups, methoxyl can often be replaced by ethoxyl by the action of sodium ethoxide, and ethoxyl by methoxyl by means of sodium methoxide. *m*-Nitro-groups do not influence the substitution, but it is facilitated by increase in the number of nitro-groups in the ortho- and para-positions.

Sodium ethoxide reacts with 2:3:4-trinitroanisole in alcoholic solution to form the diethyl ether of 2:4-dinitroresorcinol, in addition to the corresponding methyl ethyl ether, the first compound resulting from replacement of both OMe and NO<sub>2</sub> by OEt.

With an alcoholic solution of sodium ethoxide, 3-chloro-4:6-dinitroanisole and 3-chloro-2:4:6-trinitroanisole yield respectively the diethyl ether of 4:6-dinitroresorcinol and that of 2:4:6-trinitroresorcinol, both OMe and Cl being replaced by OEt. Sodium methoxide dissolved in methyl alcohol yields with the same two

compounds the corresponding dimethyl ethers, OEt and Cl being replaced by OMe.

A similar solution of sodium methoxide converts the diethyl ether of 2:4:6-trinitroresorcinol into the corresponding dimethyl ether. A small quantity of sodium dissolved in methyl or ethyl alcohol suffices to start these reactions, but they do not take place in neutral or acid solutions.

The ethyl ethers of 4:6-dinitroresorcinol, picric acid, and 2:4-dinitrophenol are converted in analogous manner into the corresponding methyl ethers by treatment with sodium methoxide dissolved in methyl alcohol, and these are reconverted into the original ethyl ethers by boiling with a solution of sodium ethoxide in ethyl alcohol.

The greater the number of nitro-groups in the para-position to the alkoxy group the more rapid the transformation, so that the ethers of 2:4:6-trinitroresorcinol and picric acid react more quickly than those of 4:6-dinitroresorcinol and 2:4-dinitrophenol. The methoxy group in *p*-nitroanisole is very stable towards sodium ethoxide (compare Luloffs, Abstr., 1902, i, 87). *m*-Nitro-groups exert no influence, so that the methoxy group in 3:5-dinitroanisole is not affected by boiling with an alcoholic solution of sodium ethoxide. The influence of the *o*- and *p*-nitro-groups is well illustrated by the transformation of the dimethyl ether of 3:5-dinitrocatechol into 3:5-dinitro-2-ethoxyanisole.

Sodium disulphide,  $\text{Na}_2\text{S}_2$ , and potassium cyanide undergo alcoholic dissociation in alcoholic solution; thus a solution of potassium cyanide in methyl alcohol converts 2:4-dinitrophenetole into 2:4-dinitroanisole, a similar solution in ethyl alcohol effecting the reverse transformation.

2:4:6-Trinitro-3-chloro-1-ethoxybenzene is converted by a solution of sodium methoxide in methyl alcohol into 2:4:6-trinitro-3-ethoxyanisole. This substance is not formed by treating 3-chloro-2:4:6-trinitroanisole with sodium methoxide, an indication that the replacement of methoxyl by ethoxyl is more readily effected than the converse transformation.

These reactions resemble those described by Lapworth (Proc., 1898, 159; 1903, 23), Meisenheimer (Abstr., 1902, i, 795), Loring Jackson and his students (Abstr., 1898, i, 517; 1900, i, 433; 1903, i, 339), and Merz and Ris (Abstr., 1886, 872). They depend on addition of sodium alkyloxy to the nitro-group, with subsequent displacement of one alkyloxy-group by another, the nature of the substituting group being dependent on the particular alcohol employed.

A. J. W.

1:5- and 1:8-Anthradiol [Rufol and Chrysazol]. BR. LAMPE (*Ber.*, 1909, 42, 1413—1418).—Recent work in this field (Abstr., 1904, i, 176, 256) has made it possible to prepare these two compounds in larger quantities than hitherto, and the author has re-investigated their properties.

Antraquinone-1:5- and -1:8-disulphonic acids were converted into the corresponding potassium anthracenedisulphonates (Abstr., 1882, 855), yield 70—80%, and these substances converted into the two dihydroxyanthracenes, rufol and chrysazol,  $\text{C}_{14}\text{H}_8(\text{OH})_2$ , respec-

tively, by fusing with potassium hydroxide; yield 80%. Rufol is a yellow, crystalline substance, m. p.  $265^{\circ}$  (decomp.), and gives a colourless diacetate and other derivatives, as described by Liebermann (Abstr., 1879, 257). Chrysazol is a pale yellow compound, m. p.  $225^{\circ}$  (decomp.), and gives a colourless, crystalline diacetyl compound, also in agreement with previous observations (Liebermann, Abstr., 1879, 537).

The alkyl ethers of these dihydroxyanthracenes were readily prepared by dissolving them in absolute alcohol, and passing a rapid current of dry hydrogen chloride through the solution warmed to about  $50-60^{\circ}$ . 1:5-*Anthradiol diethyl ether*,  $C_{14}H_8(OEt)_2$ , yield 70%, glistening needles, m. p.  $179^{\circ}$ ; the *dimethyl ether*,  $C_{14}H_8(OMe)_2$ , yield 75-80%, small, glistening plates, m. p.  $224^{\circ}$ .

When dissolved in carbon disulphide and treated with a carbon disulphide solution of bromine, the above ethers give respectively the *dibromo-derivative*,  $C_{14}H_6Br_2(OEt)_2$ , yellow needles, m. p.  $250^{\circ}$ , and  $C_{14}H_6Br_2(OMe)_2$ , yellow needles, m. p.  $302^{\circ}$ . 1:8-*Anthradiol diethyl ether*,  $C_{14}H_8(OEt)_2$ , yield 70%, brilliant plates, m. p.  $139^{\circ}$ ; the *dimethyl ether*,  $C_{14}H_8(OMe)_2$ , yield 70%, glistening plates, m. p.  $198^{\circ}$ . 1:5- and 1:8-*Anthracenedisulphonyl chlorides*,  $C_{14}H_8(SO_2Cl)_2$ , are obtained as yellow needles, m. p.  $249^{\circ}$  and  $225^{\circ}$  respectively, by treating the dry sodium salt of the anthracenedisulphonic acids with phosphorus pentachloride, and these compounds when treated with alcoholic ammonia solution give the 1:5-*disulphonamide*, m. p. above  $330^{\circ}$ , and the 1:8-*disulphonamide*, m. p.  $333^{\circ}$ . Similarly, 1:5- and 1:8-*anthracenedisulphonamides* have been prepared; they have m. p.  $293^{\circ}$  and  $224^{\circ}$  respectively.

J. V. E.

**Mechanism of the Action of Sulphur and of Selenium on Organomagnesium Derivatives.** HENRI WUYTS (*Bull. Soc. chim.*, 1909, [iv], 5, 405-412).—The author has shown that sulphur reacts with organomagnesium derivatives to form a mixture of the corresponding thiol, monosulphide, and disulphide (Abstr., 1903, i, 686; 1906, i, 257); Taboury found that only the thiol and disulphide were formed, but when selenium replaced the sulphur in the reaction, the monoselenide was one of the products (Abstr., 1903, i, 748; 1904, i, 493; 1905, i, 56, 644; 1906, i, 834; 1907, i, 837).

The author now finds that when the reaction is carried out in an atmosphere of dry hydrogen, and excess of sulphur is avoided, the thiol is the only product, and this is obtained to the extent of 80% of the theoretical quantity; the disulphide is the result of the action of sulphur on the compound formed by the condensation of the thiol with a further quantity of organomagnesium derivative according to the equations:  $R \cdot S \cdot H + R \cdot Mg \cdot X = R \cdot S \cdot MgX + R \cdot H$ ;  $2R \cdot S \cdot Mg \cdot X + S = R \cdot S \cdot S \cdot R + S(MgX)_2$ , whilst the monosulphide, as already shown (Abstr., 1906, i, 257), is formed from the interaction between the disulphide and the organomagnesium derivative:  $R \cdot S \cdot S \cdot R + RMgX = R \cdot S \cdot R + R \cdot S \cdot MgX$ . Taking the same precautions, selenophenol can be obtained to the extent of 81.2% of the theoretical quantity by the action of selenium on magnesium phenyl bromide.

The corrected boiling points of synthetic phenol, thiophenol, and

selenophenol prepared as above are phenol,  $181.3^{\circ}/760$  mm.; thiophenol,  $168.3^{\circ}/760$  mm.; selenophenol,  $183.6^{\circ}/760$  mm. M. A. W.

**Extraction of Phytosterols and Cholesterols from Fats.** A. HEIDUSCHKA and H. W. GLOTH (*Pharm. Zentr.-h.*, 1909, 50, 333—334).—One hundred grams of the fat are saponified with 200 c.c. of alcoholic potassium hydroxide (200 grams in one litre of 70% alcohol), 600 c.c. of water are added, and the solution is placed in a specially constructed cylinder. By means of a special funnel-tube, 400 c.c. of ether are poured down to the bottom of the liquid, and as the ether collects on the surface, the solution is saturated with ether without having recourse to shaking. The cylinder is attached to a flask in which 500 c.c. of ether are being boiled; the ether distillate ascends through the alkaline liquid, meanwhile dissolving the unsaponifiable matters, and collects on the surface, from which at intervals it is syphoned back into the flask. After some four hours, the extraction is complete.

L. DE K.

**Catalytic Actions of Colloidal Metals of the Platinum Group.**  
VI. Reduction Catalysis with Colloidal Palladium. CARL PAAL and JOSEF GERUM (*Ber.*, 1909, 42, 1553—1560. Compare this vol., i, 358).—An investigation on the reduction of benzonitrile, mandelonitrile, and benzaldoxime with palladium hydrosol and hydrogen at the ordinary temperature.

Benzonitrile yields benzylamine, dibenzylamine, ammonia, and a small quantity of benzaldehyde, thus: (1)  $\text{Ph}\cdot\text{CN} + \text{H}_2 = \text{CHPh}\cdot\text{NH}$ ; (2)  $\text{CHPh}\cdot\text{NH} + \text{H}_2\text{O} = \text{Ph}\cdot\text{CHO} + \text{NH}_3$ ; (3)  $3\text{Ph}\cdot\text{CHO} + 2\text{NH}_3 = (\text{CHPh}\cdot\text{N})_2\text{CHPh} + 3\text{H}_2\text{O}$ ;  $(\text{CHPh}\cdot\text{N})_2\text{CHPh} + 3\text{H}_2 = \text{CH}_2\text{Ph}\cdot\text{NH}_2 + (\text{CH}_2\text{Ph})_2\text{NH}$ .

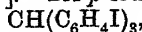
The chief products of the catalytic reduction of mandelonitrile are benzylamine, dibenzylamine, ammonia, and benzyl alcohol. The formation of these substances may be explained on the assumption that the hydroxynitrile in aqueous-alcoholic solution is partly dissociated into benzaldehyde and hydrogen cyanide. The latter substance is reduced, yielding ammonia, which combines with benzaldehyde, forming hydrobenzamide; this is then reduced to benzylamine and dibenzylamine. The benzyl alcohol is produced by the reduction of part of the benzaldehyde.

Benzaldoxime yields the same reduction products as benzonitrile. It is probable that the first product of the reduction is benzylideneimine, which undergoes further decomposition, yielding ammonia, benzylamine, dibenzylamine, and benzaldehyde in the manner already described.

W. H. G.

**Tri-halogen Substitution Products of Aromatic Compounds.**  
FRANS M. JAEGER (*Zeitsch. Kryst. Min.*, 1909, 46, 266—279).—2:4:6-Tribromobenzophenone,  $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{COPh}$ , triclinic [ $a:b:c = 1.3939:1:1.1065$ ;  $\alpha = 130^{\circ}36'$ ,  $\beta = 122^{\circ}59'$ ,  $\gamma = 58^{\circ}58'$ ]. 2:4:6-Tribromobenzonitrile, monoclinic [ $a:b:c = 1.2113:1:1.1025$ ;  $\beta = 135^{\circ}36\frac{1}{2}'$ ]. 2:4:6-Tribromobenzamide, monoclinic [ $a:b:c = 2.1655:1:1.1092$ ;  $\beta = 96^{\circ}15'$ ]. 2:4:6-Tribromobenzoyl chloride, triclinic [ $a:b:c = 1.9341:1:1.10041$ ;  $\alpha = 89^{\circ}54\frac{3}{4}'$ ,  $\beta = 108^{\circ}43\frac{3}{4}'$ ,  $\gamma = 84^{\circ}21'$ ]. 2:4:6-Tribromo-

orcinol,  $C_6Br_3Me(OH)_2$ , triclinic [ $a:b:c=1.6985:1:0.7755$ ;  $\alpha=84^\circ42'$ ;  $\beta=74^\circ33'$ ;  $\gamma=91^\circ6'$ ]. Tri-*p*-iodotriphenylmethane,



rhombic [ $a:b:c=0.5765:1:0.8798$ ]. Tri-*p*-iodotriphenylmethane + 1-benzene, triclinic [ $a:b:c=0.5719:1:1.4298$ ;  $\alpha=109^\circ8'$ ;  $\beta=126^\circ21'$ ;  $\gamma=107^\circ32'$ ]. Tri-*p*-chlorotriphenylcarbinol, rhombic [ $a:b:c=0.6009:1:0.9781$ ]. Tri-*p*-bromotriphenylcarbinol, rhombic [ $a:b:c=0.8407:1:0.8081$ ]. Tri-*p*-iodotriphenylcarbinol, rhombic [ $a:b:c=0.8543:1:0.817$ ]. Tri-*p*-iodotriphenylcarbinol + benzene, triclinic [ $a:b:c=1.3991:1:1.6135$ ;  $\alpha=109^\circ16'$ ;  $\beta=117^\circ36'$ ;  $\gamma=62^\circ52'$ ]. L. J. S.

**5-Bromo-2-aminobenzoic Acid: New Method of Preparation.** ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1909, 31, 565—569).—The present work was undertaken with the object of converting trichloroethylidene-*o*-aminobenzoic acid (chloral-anthranilic acid) (Niementowski and Orzechowski, *Abstr.*, 1896, i, 187) into a compound containing an asymmetric carbon atom. When, however, this acid is treated with a solution of bromine in glacial acetic acid, the expected asymmetric compound is not obtained, but 5-bromo-2-aminobenzoic acid *hydrobromide*, m. p. 238—240°, is produced. 5-Bromo-2-aminobenzoic acid melts at 218—219° (corr.), and its acetyl derivative at 218—220°.

When trichloroethylidene-di-*o*-aminobenzoic acid (chloral-dianthranilic acid) (Niementowski, *Abstr.*, 1903, i, 91) is similarly treated with bromine, the same product is formed. A large yield of 5-bromo-2-aminobenzoic acid hydrobromide can also be obtained by the direct bromination of anthranilic acid. This reaction affords a much more convenient method of preparing 5-bromo-2-aminobenzoic acid than that described by Alt (*Abstr.*, 1889, 987). E. G.

**Action of Aliphatic Aldehydes on Aromatic Glycines.** P. GELMO and WILHELM SUIDA (*Ber.*, 1909, 42, 1496—1502).—Formaldehyde and phenylglycine interact in cold aqueous solution, forming a yellow precipitate,  $C_{33}H_{32}O_6N_4$ , insoluble in most solvents, but dissolving in dilute acids and alkalis. It decomposes at 90—120°, giving carbon dioxide, and, when dissolved in hydrochloric acid, gives a yellow precipitate with platinum chloride. It further forms a thick, yellowish-white precipitate of a *barium* salt,  $C_{33}H_{30}O_6N_4Ba$ , and a similarly constituted dark green *copper* salt. When acetylated with acetic anhydride, carbon dioxide is eliminated, and two acetyl groups enter the molecule, forming a *compound*,  $C_{36}H_{36}O_6N_4$ . The original substance, when heated, forms a *base*,  $C_{31}H_{32}O_2N_4$ , soluble in chloroform, in which solvent the molecular-weight determination agrees with this formula. The base forms a *tetra-acetate*,  $C_{39}H_{40}O_6N_4$ , and yields with sodium nitrite an orange-red *dinitroso-compound*,  $C_{31}H_{30}O_4N_6$ .

Other aromatic glycines react with formaldehyde in a similar manner. The product from phenylmethylglycine has the composition  $C_{37}H_{40}O_6N_4$ . *p*-Tolylglycine, oxanilic acid, phenylacetic acid, phenoxylacetic acid, and hippuric acid do not react with formaldehyde under these conditions. E. F. A.

**Isomeric Cinnamic Acids. II.** EINAR BILLMANN (*Ber.*, 1909, 42, 1443—1450. Compare this vol., i, 155; also Liebermann, *ibid.*, 155).—Further experiments have confirmed the view that the two

*isocinnamic acids* and *allo-cinnamic acid* are trimorphous. It is shown that although the three acids have different m. p.'s, they form the same melt, which is the liquid form of all three, and which of the three solids is formed on cooling depends largely on the conditions of the experiment, rapid cooling tending to yield one acid only. Thus the *allo-acid* when fused and then cooled rapidly yields the *iso-acid*, m. p.  $42^{\circ}$ , when only small amounts are used, but with larger quantities the *allo-acid*, m. p.  $68^{\circ}$ , is formed. It is not necessary to heat the acids much above their respective m. p.'s in order to obtain the common melt; the process is not one of rearrangement within the molecule; the important factor is the process of fusion. The acid m. p.  $42^{\circ}$  is comparatively stable, and can be kept for several months in flasks plugged with cotton wool.

The *allo-acid* can be transformed into the *iso-acid*, m. p.  $58^{\circ}$ , by fusion, then solution of the melt in light petroleum,  $60-70^{\circ}$  (10 parts), and allowing the solution to cool in a flask provided with a cotton-wool plug. In removing the crystals it is essential that filter-paper and apparatus should be sterile (free from particles of *allo-acid*).

If the solutions are too dilute, the *allo-* and not the *iso-acid* frequently separates. The *iso-acid* m. p.  $58^{\circ}$  can also be obtained readily from the *allo-acid* by solution in light petroleum and impregnation.

J. J. S.

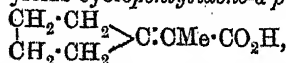
Terpenes and Ethereal Oils. XCIX. Preparation of Unsaturated Cyclic Acids and Hydrocarbons with a Semi-cyclic Linking. OTTO WALLACH (*Annalen*, 1909, 365, 255—277. Compare this vol., i, 399).—It has been shown that in the elimination of water from nopinol-acetic acid, the nature of the dehydrating agent has a marked influence on the course of the reaction (Abstr., 1908, i, 997). It is found as a result of further investigations on this subject that the hydroxy-acids or esters resulting from the condensation of the simple cyclic ketones with ethyl bromoacetate and zinc when treated with potassium hydrogen sulphate or phosphoric oxide yield chiefly unsaturated acids with the ethylene linking in the cyclic nucleus, whereas when the hydroxy-acids are boiled with acetic anhydride the tendency is for the water to be eliminated with the formation of a semi-cyclic linking. For example, ethyl *cyclohexanolacetate* when treated with potassium hydrogen sulphate or phosphoric oxide is almost completely converted into ethyl  $\Delta^1$ -*cyclohexeneacetic acid* (Wallach and Isaac, Abstr., 1906, i, 176), whilst *cyclohexanolacetic acid* when boiled with acetic anhydride yields principally  $\Delta^{\alpha}$ -*cyclohexeneacetic acid* (Abstr., 1907, i, 616). 4-Methyl*cyclohexane-1-ol-1-acetic acid* behaves in an exactly analogous manner. It is found, as a general rule, that the acid with the semi-cyclic linking has a higher m. p. than the isomeride with the ethylene linking in the nucleus. Further, an acid with a semi-cyclic linking when heated alone yields the same hydrocarbon as the isomeric acid containing the ethylene linking in the nucleus, thus upholding the statement made previously that there is a tendency for unsaturated cyclic acids with an ethylene linking in the nucleus to yield hydrocarbons with a semi-cyclic linking (Abstr., 1908, i, 402).

Although many of the esters of hydroxy-acids formed by the condensation of ketones with halogenated acid esters and zinc when hydrolysed do not yield the hydroxy-acid, but are further dissociated, it is found that the simple cyclic hydroxy-acids, such as *cyclopentanolacetic acid*, *cyclohexanolacetic acid*, *p*-methyl*cyclohexanolacetic acid*, and the corresponding propionic acids, may be obtained by hydrolysing the respective esters. In all cases hitherto studied, it is found that the esters which when hydrolysed break down readily, when heated dissociate into ketone and aliphatic acid, whilst the hydroxy-acids which are found to be stable during their formation from the esters by hydrolysis, when distilled slowly break down into water and an unsaturated acid, which decomposes slightly, yielding carbon dioxide and a hydrocarbon. For example,  $\alpha$ -mentholpropionic acid yields menthone and propionic acid, whilst *cyclohexanolacetic acid* decomposes into water, carbon dioxide, and chiefly methylenecyclohexane. The conversion of an unsaturated hydrocarbon with a semi-cyclic linking into a ketone containing an ethylene linking in the nucleus has hitherto been performed only with hexacyclic compounds; the formation of acetyl- $\Delta^1$ -cyclopentene ( $\Delta^1$ -cyclopentene methyl ketone) from *cyclopentanone* is described in the present paper.

4-Methyl*cyclohexane*-1-ol-1-acetic acid, m. p.  $141^\circ$ , or  $89-90^\circ$  (compare Wallach and Evans, Abstr., 1906, i, 566), when boiled with acetic anhydride yields 1-methyl*cyclohexylidene*-4-acetic acid, m. p.  $63-64^\circ$ . Perkin and Pope give m. p. about  $70^\circ$  (Trans., 1908, 93, 1084); the *amide* forms glistening leaflets, m. p.  $121-122^\circ$ . The acid when distilled yields 1-methyl-4-methylenecyclohexane, identical with the hydrocarbon obtained from methyl- $\Delta^4$ -cyclohexeneacetic acid (Wallach and Evans, loc. cit.).

[With MARLON RENTSCHLER.]—1-Methyl*cyclohexane*-1-ol-1- $\alpha$ -propionic acid,  $\text{CHMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C}(\text{OH}) \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ , obtained by hydrolysing the ethyl ester, crystallises in two modifications; the less soluble form has m. p.  $110-111^\circ$ ; the more soluble variety has a lower m. p. The acid, m. p.  $110-111^\circ$ , when heated with acetic anhydride yields 1-methyl*cyclohexylidene*-4- $\alpha$ -propionic acid, obtained as a viscid liquid, which when distilled slowly in hydrogen yields 1-methyl-4-ethylidene-cyclohexane, b. p.  $152-153^\circ$ ,  $D_{25}^{25}$  0.810,  $n_D^{25}$  1.4571 (compare Wallach and Evans, Abstr., 1908, i, 404). The same hydrocarbon is more readily obtained by the dry distillation of 1-methyl*cyclohexane*-1-ol-1- $\alpha$ -propionic acid. The nitroschloride derived from the hydrocarbon has m. p.  $108-110^\circ$ .

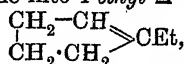
[With KURT VON MARTIUS.]—Ethyl *cyclopentane*-1-ol-1- $\alpha$ -propionate,  $\text{CH}_2 \cdot \text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C}(\text{OH}) \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$ , obtained by the action of zinc and ethyl  $\alpha$ -bromopropionate on *cyclopentanone*, yields on hydrolysis the crystalline acid, m. p.  $58-59^\circ$ . The latter substance when heated with acetic anhydride yields *cyclopentylidene*- $\alpha$ -propionic acid,



a crystalline substance, m. p.  $107-108^\circ$ , which when distilled yields

chiefly *ethylidenecyclopentane*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C} : \text{CHMe}$ , a colourless liquid, b. p. 113—117°, D 0.8020,  $n_D^{20}$  1.4481. The *nitrosochloride* when heated with alcoholic piperidine forms a *nitrolpiperidide*, m. p. 110°, and when boiled with glacial acetic acid and sodium acetate yields the *oxime* of *acetylcyclopentene*, m. p. 90—91°. The latter substance when hydrolysed yields *acetylcyclopentene* (compare Perkin and Wallach, this vol., i, 154).

1-*Ethylcyclopentane-1-ol*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CEt} \cdot \text{OH}$ , prepared from *cyclopentanone* by Grignard's reaction, is a colourless liquid with a camphor-like odour, b. p. 155—157°, D 0.916,  $n_D^{20}$  1.4528. It is converted on treatment with zinc chloride into 1-*ethyl- $\Delta^1$ -cyclopentene*,



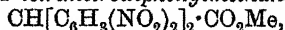
a colourless liquid, b. p. 107—110°, D 0.7975,  $n_D^{20}$  1.4426, which yields a *nitrosochloride*, from which an oily *oxime* was prepared. The latter when hydrolysed gave a substance which is probably 1-*ethyl- $\Delta^1$ -cyclopentene-2-one*.  
W. H. G.

#### Ethyl $\alpha$ -Dinitrophenylacetoacetate and Related Compounds.

II. WALTHER BORSCHKE (*Ber.*, 1909, 42, 1310—1318. Compare this vol., i, 232).—The investigation was undertaken with the object of comparing the reactions of the esters of nitroarylacetic acids with those of  $\beta$ -ketonic acids, in view of the analogy which subsists between the nitro-substituted aryl group,  $(\text{NO}_2)_x \text{Ar}^-$ , and the acid radicle,  $\text{RCO}^-$ , as shown in the acid character of their corresponding hydroxyl derivatives, the nitrophenols, and the carboxylic acids. The present communication contains an account of the reactions of methyl dinitrophenylacetate with benzoyl chloride, nitrous acid, and certain aromatic aldehydes.

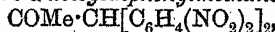
2:4-Dinitrophenylacetic acid, prepared by nitrating phenylacetic acid with a mixture of nitric and sulphuric acids below 60°, has m. p. 179—180°, and not 160°, as stated.

By acting on methyl sodiodinitrophenylacetate with benzoyl chloride and hydrolysing the resulting product with dilute sulphuric acid, a 40% yield of  $\omega$ -2:4-dinitrophenylacetophenone is obtained. When treated with bromo-2:4-dinitrobenzene, the sodium derivative above-mentioned gives *methyl 2:4:2':4'-tetranitrodiphenylmethane- $\alpha$ -carboxylate*,



which crystallises from a mixture of chloroform and methyl alcohol in rhombic plates, m. p. 159°.

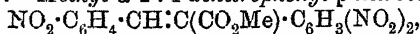
2:4:2':4'-*Tetranitro- $\alpha$ -acetyldiphenylmethane*,



obtained by acting on the sodium derivative of dinitrophenylacetone with bromodinitrobenzene, crystallises from ethyl acetate in yellow, glistening needles, m. p. 183° (decomp.).

*Methyl 5-nitrobenzisoaxazole-2-carboxylate*,  $\begin{array}{c} \text{O} - \text{C}_6\text{H}_4 \cdot \text{NO}_2 \\ | \\ \text{N} = \text{C} \cdot \text{CO}_2\text{Me} \end{array}$ , is obtained by shaking a mixture of methyl dinitrophenylacetate and *isoamyl nitrite*

with sodium and methyl alcohol; it crystallises from methyl alcohol in yellowish-white, glistening needles, m. p. 130—131°. On substituting ethyl alcohol for methyl alcohol, the corresponding *ethyl* ester is obtained, which crystallises from ethyl alcohol in yellow leaflets, m. p. 101—102°. *Methyl α-2:4-dinitrophenyl-p-nitrocinnamate*,



is prepared by heating methyl dinitrophenylacetate with nitrobenzaldehyde and a few drops of piperidine at 150° for twenty minutes; it separates from a mixture of ethyl acetate and alcohol in light brown needles, m. p. 169—170°.

*3-o-p-Dinitrophenylcoumarin*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}=\text{C} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \text{O} \quad \text{CO} \end{smallmatrix}$ , obtained

in a similar manner by the interaction of methyl dinitrophenylacetate and salicylaldehyde in presence of piperidine, crystallises from a large volume of glacial acetic acid in glistening plates, m. p. 249—250°.

*3-o-p-Dinitrophenylcarbostyryl*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}=\text{C} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2 \\ \text{NH}-\text{CO} \end{smallmatrix}$ , prepared

by condensing the ester with α-aminobenzaldehyde at 180°, crystallises from glacial acetic acid in dark yellow, glistening crystals; it is not visibly altered by heating to 270°. P. H.

**Hydrophthalic Acids. VII. Resolution of the Racemic Form of the Fumaroid Δ<sup>4</sup>-Tetrahydrophthalic Acid.** GINO ABATI and CESARE DE HORATIIS (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 218—223. Compare this vol., i, 104).—According to von Baeyer, whose extension of Le Bel and van't Hoff's theory to hydrogenated phthalic acids has recently received confirmation (Abstr., 1900, i, 100), *trans*-Δ<sup>4</sup>-tetrahydrophthalic acid should be capable of existing in two optically antipodal forms. Attempts to effect separation of these forms by means of the quinine salts have led to the isolation of two acids: (1) that obtained from the less soluble (in 96% alcohol) quinine salt, which has  $[\alpha]_D^{25} + 115.2^\circ$ ; and (2) the one corresponding with the more soluble quinine salt, and having  $[\alpha]_D^{25} - 97.4^\circ$ . This difference between the arithmetic magnitudes of the two rotations is explained by the fact that the acid obtained by the reduction of phthalic acid is pseudo-racemic, its rotation being  $[\alpha]_D^{25} + 2.9^\circ$ , and that of its anhydride,  $[\alpha]_D^{25} 4.17^\circ$ . The anhydride of the dextrorotatory Δ<sup>4</sup>-tetrahydrophthalic acid has  $[\alpha]_D^{25} + 6.6^\circ$ .

T. H. P.

**Hydrophthalic Acids. VIII. Influence of Presence and Position of the Ethylene Grouping on the Refraction and Dispersion of Hydrophthalic Anhydrides.** GINO ABATI and ERNESTO VERGARI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 223—234).—The authors have measured the rotations and dispersions of phthalic anhydride, of the various di-, tetra-, and hexa-hydrophthalic anhydrides, and of citraconic and itaconic anhydrides, in order to ascertain whether the laws of Brühl concerning the rotations and dispersions of compounds containing two neighbouring groups of high refractive power (Trans., 1907, 91, 115) hold for these compounds.

The results obtained directly contradict Brühl's laws. Thus, for the tetrahydrogenated derivatives, the molecular refraction should be greatest for the  $\Delta^1$ -anhydride, and should diminish as the distance of the ethylene group from the carbonyls increases; in reality, however, the values for the  $\Delta^1$ - and  $\Delta^2$ -compounds are slightly below, and the value for the  $\Delta^3$ -compound slightly above, the theoretical value.

The most striking feature of the results is the great differences between the refractions of stereoisomerides, in each of the three cases examined the fumaroid derivative having an appreciably higher molecular refraction than the maleinoid form. The difference amounts to 2.68 for the  $\Delta^{3:5}$ -dihydro-acid, to 5.08 for the  $\Delta^4$ -tetrahydro-anhydride, and to 0.75 for the hexahydroanhydride. In nearly all the cases previously observed, the fumaroid isomeride has slightly the higher refraction.

The specific dispersion does not always correspond with the refraction for the line  $H_\alpha$ . Excepting with the four dihydrophthalic anhydrides, where parallelism exists, in none of the cases is there any relation with the constitution of the compounds of the kind formulated by Brühl (*loc. cit.*).  
T. H. P.

**Gentisic Acid (2:5-Dihydroxybenzoic Acid) and Derivatives.** FRANZ VON HEMMELMAYR (*Monatsh.*, 1909, 30, 255—269).—By the action of bromine on gentisic acid, a monobromogentisic acid is formed; excess of bromine eliminates the carboxyl group, forming bromo-anil, and a dibromogentisic acid could not be obtained. The isomeric dihydroxybenzoic acids yield dibromo-derivatives. By the action even of excess of methyl iodide and sodium methoxide, bromogentisic acid monoethyl ether is obtained; in this, probably the hydroxyl in the meta-position to the carboxyl group is methylated. When sodium hydroxide in methyl-alcoholic solution is employed, it is possible also to some extent to methylate the second hydroxyl. When heated at 160° in presence of water, bromoquinol is formed from the bromogentisic acid, which probably has the composition  $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \diagup \text{C(OH):CBr} \\ \diagdown \text{CH-C(OH)} \end{smallmatrix} \text{CH}$ .

Nitric acid has an oxidising action on gentisic acid; only when very dilute acid is employed was evidence of the formation of a nitro-compound obtained. Nitric acid also acts only as an oxidising agent towards bromo- and diacetyl-gentisic acids.

*Bromogentisic acid* forms colourless needles, m. p. 238°, which show a blue coloration with ferric chloride. The *barium* salt forms faintly rose-coloured tablets; the *silver* salt separates in colourless needles; the *methyl* ester crystallises in glistening plates, m. p. 135°, and gives a greenish-blue coloration with ferric chloride.

*Bromogentisic acid monomethyl ether* has m. p. 194°, and gives an intense blue ferric chloride coloration; the *barium* salt forms needles, grouped in feather-like clusters.

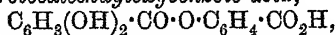
*Bromogentisic acid dimethyl ether* crystallises in needles, m. p. 122°. *Diacetylgentisic acid* forms colourless crystals, m. p. 118—119°.

E. F. A.

**Derivatives of Protocatechuic Acid.** TOKUHEI KAMETAKA (*Ber.*, 1909, 42, 1482—1485).—By the interaction of dimethyl-

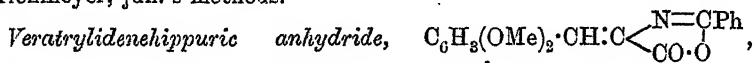
carbonatoprotocatechuy chloride and ethylglycine in ethereal solution, *ethyl dimethylcarbonatoprotocatechuyglycine* is obtained as a colourless syrup. On hydrolysis with sodium hydroxide, 3:4-*dihydroxyhippuric acid*,  $C_6H_3(OH)_2 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , is formed, crystallising in colourless prisms, m. p. 228° (corr. with decomp.).

*p-Dimethylcarbonatoprotocatechuyloxybenzoic acid* forms a crystalline precipitate, which, when heated, softens at 165°, sinters at 180°, m. p. 187·5° (corr.). *p-Protocatechuyloxybenzoic acid*,

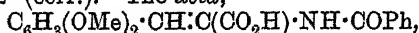


forms microscopic, colourless needles, aggregated in balls, m. p. 270° to a brown liquid. E. F. A.

**Derivatives of Benzylphenacetic Acid.** WALTER KROPP and HERMAN DECKER [and, in part, CLEMENS ZOELLNER] (*Ber.*, 1909, 42, 1184—1192).—Various *isoquinoline* derivatives closely related to certain natural alkaloids have been synthesised by Plöchl and Erlenmeyer, jun.'s methods.

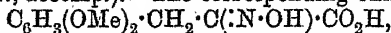


obtained by heating methylvanillin and hippuric acid with acetic anhydride and anhydrous sodium acetate, is purified by extracting with cold alcohol and boiling water, and crystallises from benzene in yellow plates, m. p. 152° (corr.). The *acid*,



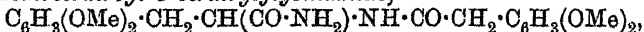
is obtained by boiling the anhydride with 2% sodium carbonate solution and precipitating the clear solution with a mineral acid. It crystallises from hot alcohol in prisms, m. p. 213° (corr.). The *methyl ester*,  $C_{19}H_{19}O_5N$ , crystallises from methyl alcohol in transparent plates, m. p. 147° (corr.).

3:4-*Dimethoxyphenylpyruvic acid*,  $C_6H_3(OMe)_2 \cdot CH_2 \cdot CO \cdot CO_2H$ , obtained by boiling the anhydride for four hours with 10% sodium hydroxide solution, acidifying, and removing the benzoic acid by steam distillation, crystallises from glacial acetic acid in colourless plates, m. p. 187° (corr., decomp.). The corresponding oxime,

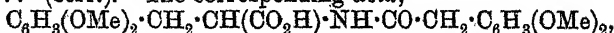


crystallises from hot water in slender needles, m. p. 165° (decomp.).

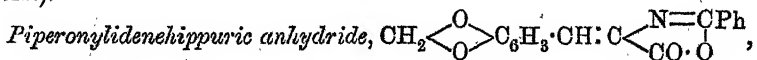
*N-Homoveratroyl-C-veratrylglycinamide*,



obtained by heating the ketonic acid with aqueous ammonium hydroxide solution at 100°, crystallises from water in needles, m. p. 176—177° (corr.). The corresponding *acid*,

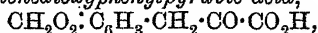


prepared by hydrolysing the amide with sodium hydroxide solution, also crystallises from water in colourless needles, m. p. 156—157° (corr.).



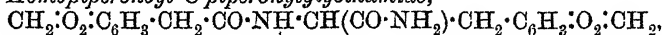
crystallises from benzene in yellow, flat needles, m. p. 197·4° (corr.). The corresponding *acid*,  $C_{17}H_{15}O_5N$ , turns yellow at 200°, and decomposes and melts at about 235° (corr.). The *methyl ester*,  $C_{18}H_{15}O_5N$ ,

crystallises from methyl alcohol, and has m. p.  $151^{\circ}$  (corr.). At a slightly higher temperature decomposition begins, and in all probability the anhydride is re-formed. The *ethyl* ester,  $C_{19}H_{17}O_5N$ , has m. p.  $136^{\circ}$  (corr.). *Methylenedioxyphenylpyruvic acid*,



crystallises from glacial acetic acid in plates, m. p.  $215^{\circ}$  (decomp.). The *oxime*,  $CH_2O_2 \cdot C_6H_3 \cdot CH_2 \cdot C(N \cdot OH) \cdot CO_2H$ , crystallises from water, and has m. p.  $170-171^{\circ}$  (decomp.).

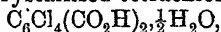
*N-Homopiperonyl-C-piperonylglycinamide*,



crystallises from alcohol in needles, m. p.  $189.5^{\circ}$  (corr.), and the corresponding *acid*,  $C_{19}H_{17}O_7N$ , crystallises from a mixture of benzene and alcohol in stellar aggregates of needles, m. p.  $179^{\circ}$  (corr.).

J. J. S.

**Tetrachlorophthalic Acid.** T. G. DELBRIDGE (*Amer. Chem. J.*, 1909, 41, 393—417).—Crystallised tetrachlorophthalic acid,



has been described by previous authors as anhydrous; when heated to  $109^{\circ}$ , it is completely converted into tetrachlorophthalic anhydride; hence the observed melting point ( $255-257^{\circ}$ ) is in reality that of the pure anhydride; the m. p.'s of the acid and its anhydride are stated by previous workers to be  $250^{\circ}$  and  $245^{\circ}$  respectively. Anhydrous tetrachlorophthalic acid is formed when the acid is crystallised from acetone; a compound containing two molecules of acetone is hereby produced, which, in a current of dry air, loses all its acetone, leaving anhydrous tetrachlorophthalic acid; this anhydrous acid takes up moisture from the air to form the stable acid containing  $\frac{1}{2}H_2O$ .

P. H.

**Tetrachlorophenolphthalein and Some of its Derivatives.** WILLIAM R. ORNDORFF and JOHN A. BLACK (*Amer. Chem. J.*, 1909, 41, 349—393).—Tetrachlorophenolphthalein (compare Graebe, *Abstr.*, 1887, 832) can be prepared by heating a mixture of tetrachlorophthalic anhydride, fuming sulphuric acid containing 15% of sulphur trioxide, and phenol for twelve hours at  $145-150^{\circ}$ ; 65% of the tetrachlorophthalic acid is thereby converted into the tetrachlorophthalein and 10% into tetrachlorofluoran; it crystallises from dilute alcohol in slender needles and from methyl alcohol in monoclinic crystals, and does not melt at  $300^{\circ}$ ; it dissolves in alkali hydroxides or carbonates; in concentrated solution the colour is red, in thin layers purple, whilst in dilute solution it is violet-red; in very dilute alkaline solution the colour has a bluish tint, which distinguishes it from phenolphthalein.

Tetrachlorofluoran,  $O \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} C \begin{smallmatrix} \diagup O \diagdown \\ \diagdown C_6Cl_4 \diagup \end{smallmatrix} CO$ , obtained as stated above, crystallises from benzene in triclinic prisms; it does not melt at  $300^{\circ}$ .

*Tetrachlorodiacetylphenolphthalein*,  $C_{20}H_8O_4Cl_4Ac_2$ , prepared by heating the tetrachlorophenolphthalein with acetic anhydride and sodium acetate, separates from alcohol in monoclinic crystals, and has m. p.  $205-206^{\circ}$ .

*Tetrachlorophenolphthalein methyl ether*, obtained by heating tetrachlorophenolphthalein with sodium in absolute methyl alcohol and methyl iodide for three hours, separates from acetone in monoclinic or triclinic scales; it does not melt at 300°.

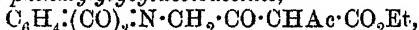
The *dimethyl ether*, obtained by heating the same mixture for 120 hours, is colourless; it forms flattened needles from alcohol, m. p. 152—153°.

*Tetrachlorotetrabromophenolphthalein*, obtained by adding bromine dissolved in glacial acetic acid to a boiling alcoholic solution of tetrachlorophenolphthalein, separates from benzene in colourless crystals, and does not melt at 300°; it is a stronger acid than tetrachlorophenolphthalein or phenolphthalein, but, like these substances, is sensitive to carbonic acid and cannot therefore be used for titrating carbonates. Its *diacetate*, m. p. 190—191°, crystallises from benzene; the *di-ammonium* salt is an unstable, blue compound; the *disilver* salt was also prepared.

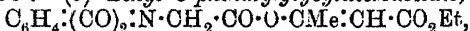
*Tetrachlorotetrabromophenolphthalein dimethyl ether* is a colourless substance, which separates from benzene in triclinic crystals, m. p. 265—266°; the *diethyl ether*, colourless crystals from benzene, m. p. 201—202°.

Tetrachlorophenolphthalein and tetrachlorotetrabromophenolphthalein can be used as indicators for titrating organic acids or alcoholic solutions; neither of them is esterified by alcohol and hydrochloric or sulphuric acid. P. H.

**Action of Phthalylglycyl Chloride on Ethyl Sodiacetoacetate.** JOHANNES SCHEIBER (*Ber.*, 1909, 42, 1441—1443).—The products obtained by the action of a benzene or ethereal solution of phthalylglycyl chloride on the sodium derivative of ethyl acetoacetate are: (a) *Ethyl O-phthalylglycylacetoacetate*,



which crystallises from boiling alcohol in brilliant, colourless prisms, m. p. 135—136°. (b) *Ethyl O-phthalylglycylacetoacetate*,



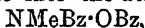
which forms colourless crystals, m. p. 97—98°. (c) *Ethyl diphtalylglycylacetoacetate*,  $\text{CAc}(\text{CO}\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{O}_2\cdot\text{C}_6\text{H}_4)_2\cdot\text{CO}_2\text{Et}$ , long needles from alcohol, m. p. 158—159°. High temperatures favour the formation of a, and working in the cold the formation of b and c, but the yields are poor in all cases. J. J. S.

**Oximino-compounds.** ERNST BECKMANN (*Annalen*, 1909, 365, 201—214).—Hitherto, aldoximes prepared by the action of free hydroxylamine on various aldehydes have been converted into the corresponding  $\beta$ -modifications by subsequent treatment with hydrogen chloride. It is now found that many aldehydes, for example, benzaldehyde, anisaldehyde, and cuminaldehyde, are converted directly into the hydrochlorides of the  $\beta$ -aldoximes by warming with hydroxylamine hydrochloride in alcohol. It is not possible, however, to obtain isomerides by this new method of preparation if they have not been prepared already by the older method; for example, salicylaldoxime and acetophenoneoxime prepared by this method were found

to be identical with the compounds obtained by other methods;  $\beta$ -modifications were not formed. The hydrochlorides of the  $\beta$ -aldoxime-*N*-ethers may also be prepared directly from the aldehydes by acting on these with *N*-alkylhydroxylamine hydrochlorides. The following substances were prepared by this method: *N*-phenylbenzaloxime, *N*-phenylanisaldoxime, *N*-methylbenzaloxime, *N*-methylanisalaldoxime, *N*-methylsalicylalaldoxime, *N*-methyl-*p*-hydroxybenzaloxime, and *N*-methylcuminalaldoxime. The isomeric *N*-methylbenzaloximes investigated by Luxmoore (Trans., 1896, 69, 177) are not stereoisomerides (compare Scheiber, following abstract).

[With HANS NETSCHER.]—*N*-Methylanisalaldoxime forms colourless crystals, m. p. 76° (compare Scheiber, *loc. cit.*); the hydrochloride forms white crystals, m. p. 183°. Phenylcarbimide acts on the oxime ether, yielding the carbanilido-derivative,  $C_{16}H_{16}O_3N_2$ , m. p. 85°. *N*-Methylsalicylalaldoxime,  $C_8H_9O_2N$ , forms white crystals, m. p. 134—135°; the hydrochloride has m. p. about 140°. *p*-Hydroxy-*N*-methylbenzalaldoxime is obtained as a white, crystalline powder, m. p. 220° (decomp.). *N*-Methylcuminalaldoxime,  $C_{11}H_{15}ON$ , crystallises in glistening, silvery leaflets, m. p. 65°; the hydrochloride is extremely deliquescent.

*N*-Methylhydroxylamine reacts with acetophenone and acetobenzophenone, but crystalline products could not be isolated; a crystalline substance, m. p. 114°, was obtained with acetone, and acetylacetone also yields a crystalline substance, m. p. 65°. *N*-Methylhydroxylamine is converted by phenylcarbimide into  $\beta$ -carbanilido-*N*-methylhydroxylamine, m. p. 96—98° (compare Kjellin, Abstr., 1894, i, 9), and by benzoyl chloride into the dibenzoyl derivative,



colourless crystals, m. p. 56°.

W. H. G.

**Appearance of Stereoisomerism in *N*-Substituted Aldoximes.** JOHANNES SCHEIBER (*Annalen*, 1909, 365, 215—239).—Evidence of the existence of stereoisomerides of only two *N*-substituted aldoximes has been published up to the present, although about 140 *N*-substituted aldoximes are known. Of the two cases, that investigated by Luxmoore (Trans., 1896, 69, 177) appeared to be founded on the more weighty evidence. It seemed desirable, therefore, to investigate this subject more thoroughly, and as a result it is found that the supposed stereoisomeric *N*-methylbenzalaldoxime described by Luxmoore is really a monohydrated form of the *N*-methylbenzalaldoxime described originally by Goldschmidt and Kjellin (Abstr., 1891, 1477).

Attempts to obtain two modifications of *N*-benzylbenzalaldoxime and *N*-methylanisalaldoxime were unsuccessful. The existence of two forms of the latter compound appeared probable, since a *N*-methylanisalaldoxime prepared by Goldschmidt (Abstr., 1892, 974) had m. p. 45°, whilst that described by Beckmann and Netscher (preceding abstract) had m. p. 76°. However, in this case, also, the compound with the lower m. p. was found to be a hydrated form of *N*-methylanisalaldoxime, m. p. 76°. Similarly, although two hydrobromides were prepared from *N*-methylanisalaldoxime, it was found that the one was a hydrated form of the other.

[With H. FLEISCHMANN and RUDOLF FLEBE.]—*N*-Methylbenzaldoxime hydrobromide is most readily prepared by the action of methylhydroxylamine hydrobromide on benzaldehyde in alcohol. Contrary to Luxmoore's statement, the hydrobromide prepared by the action of methyl bromide on benzalaldoxime is identical with that obtained by the action of hydrogen bromide on *N*-methylbenzaldoxime; it is a *monohydrate*,  $C_8H_9ON, HBr, H_2O$ , m. p. 67—68°, and passes into the *anhydrous* salt,  $C_8H_9ON, HBr$ , m. p. 124°, when kept in a vacuum desiccator. A *hydrobromide*,  $C_8H_9ON, HBr$ , m. p. 85°, is obtained by treating a solution of the aldoxime in a perfectly dry mixture of benzene and ether with hydrogen bromide. It yields the monohydrate when crystallised from ether and alcohol.

The hydrobromide, m. p. 67°, when treated with ammonia in alcoholic solution, yields an oil which is, without doubt, the hydrated form of the *N*-ether; a small quantity of the *O*-methyl ester is also formed at the same time. The substance, m. p. 45—49°, described by Luxmoore was never obtained. The oily substance obtained initially becomes semi-solid when kept, owing to the separation of the *N*-methyl ether, m. p. 81—82°.

*N*-Methylbenzaldoxime hydrochloride,  $C_8H_9ON, HCl$ , is extremely hygroscopic, and only when perfectly dry has m. p. 140°; the *hydrate*,  $C_8H_9ON, HCl, H_2O$ , has m. p. 95—100°.

*N*-Methylanisaloxime has m. p. 76° (compare Beckmann and Netscher, *loc. cit.*); it rapidly absorbs water from the air, passing into the *hydrate*,  $C_9H_{11}O_2N, H_2O$ , m. p. about 45°, which is probably identical with the *N*-methylanisaloxime described by Goldschmidt (*loc. cit.*). The *hydrobromide*,  $C_9H_{11}O_2N, HBr$ , has m. p. 170°; the *hydrate* ( $1H_2O$ ) has m. p. 136°. Attempts to prepare a hydrated form of the hydrochloride were fruitless.

W. H. G.

**The Aldehyde Reaction.** ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 376—378. Compare this vol., i, 308).—The authors describe experiments made with the view of determining the influences of the solvent and of the experimental conditions on the addition of dihydroxyammonia to aldehydes and to true nitroso-derivatives (compare Jeanrenaud, *Abstr.*, 1889, 870).

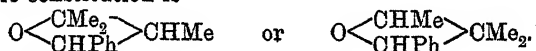
With a sulphhydroxamic acid and an aldehyde, four reactions are possible: (1)  $R \cdot SO_2 \cdot NH \cdot OH + H_2O = R \cdot SO_2H + NH(OH)_2$ ; (2)  $R \cdot CHO + NH(OH)_2 = OH \cdot CR \cdot N \cdot OH + H_2O$ ; (3)  $2NH(OH)_2 = N_2O + 3H_2O$ , and (4)  $nR \cdot CHO = (R \cdot CHO)_n$ , the yield of hydroxamic acid depending on the velocity of reaction (2). With aliphatic and aromatic aldehydes and their ethers, this reaction is almost instantaneous, and gives good yields in either aqueous or alcoholic solution; with certain unsaturated aldehydes it is slower. Ortho-substitution in aromatic aldehydes, in general, retards the reaction, and in some cases completely stops it. When alcohol is used as solvent, the reaction takes place more readily, so that a good yield of *m*-hydroxybenzhydroxamic acid (*loc. cit.*) may be obtained, provided the calculated proportion of potassium hydroxide is added gradually. Under the

same conditions, salicylhydroxamic acid is obtained in small yield, whilst in aqueous solution the reaction takes place neither with benzenesulphydroxamic acid nor with the sodium salt of nitrohydroxylaminic acid; in the latter cases, the abundant evolution of nitrous oxide shows that the change is mainly according to equation (3).

Even in alcoholic solution it is found impossible to obtain hydroxamic acids from aromatic aldehydes containing a hydroxyl in the para-position, although the alkyl ethers of these *p*-hydroxyaldehydes behave normally.

T. H. P.

**Organic Syntheses by means of Sunlight. II.** EMANUALE PATERNÒ and G. CHIEFFI (*Gazzetta*, 1909, 39, i, 341–361).—The compound obtained from benzaldehyde and amylene (or  $\beta$ -methyl- $\Delta^2$ -butylene) (this vol., i, 240) has the formula  $C_{15}H_{22}O$ , is a limpid, colourless, highly refractive liquid,  $D_0$  0.9855, b. p. 230–232° (decomp.),  $n_D$  1.50710, and has the normal molecular weight (157.0–168.7, instead of 176) in freezing benzene. When oxidised with permanganate, it gives benzoic acid, whilst reduction with phosphorus and iodine yields a *hexylbenzene*,  $C_{12}H_{18}$ , b. p. 175–180°. Its probable constitution is



With anisaldehyde under the influence of sunlight, amylene yields a hydroanisoin, and an *additive* compound, b. p. 260–300° (decomp.); with valeraldehyde, the reaction is complicated by the formation of polymerides of amylene.

The product of the interaction of benzaldehyde and octylene yields two fractions, b. p. 275–300° and 300–340°, which give analytical numbers corresponding closely with an additive compound,  $C_{15}H_{22}O$ .

The compound of benzophenone and amylene (*loc. cit.*),  $O < \begin{array}{c} \text{CPh}_2 \\ \text{C}_5\text{H}_{10} \end{array}$ , m. p. 110–111°, b. p. 305–310° (decomp.), separates from alcohol in large, transparent, monoclinic crystals [*ZAMBONINI*:  $a:b:c = 0.3707:1:0.3692$ ;  $\beta = 103^\circ 23'$ ]. This compound is very stable towards the action of oxidising agents, bromine converting it into benzopinacolin; on reduction with hydriodic acid, it yields an oily hydrocarbon,  $C_{18}H_{22}$ , b. p. 281–283°.

The compound obtained from acetophenone and amylene (*loc. cit.*),  $C_{13}H_{18}O$ , is a transparent liquid, b. p. 232–233°,  $D_0$  0.9792;  $n_D$  1.50710. Amylene also yields *additive* compounds with benzylidenacetone, b. p. 320–340°, with benzoylacetone, b. p. about 300°, and with hexyl acetylmethyl ketone, b. p. above 280°.

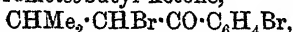
Additive compounds are also formed with hexylene, octylene, hexadecylene, and benzophenone, but here the ketone undergoes reduction to benzopinacone by the higher homologue of amylene, so that the additive compounds are probably formed from hydrocarbons containing two double linkings.

Amylene does not react under the influence of sunlight with hydrocarbons, phenols, alcohols, aceto- and benzo-nitriles, pyridine, piperidine, and organic acids.

T. H. P.

**Action of Alkali Hydroxides on  $\alpha$ -Bromo-ketones.** ELMER P. KOHLER (*Amer. Chem. J.*, 1909, 41, 417—430).—Potassium hydroxide reacts with  $\alpha$ -bromo-ketones to form either unsaturated ketones or  $\alpha$ -hydroxy-ketones, as illustrated by the two equations:

(i)  $\text{CHPh}_2 \cdot \text{CPhBr} \cdot \text{COPh} + \text{KOH} = \text{CPh}_2 \cdot \text{CPh} \cdot \text{COPh} + \text{KBr} + \text{H}_2\text{O}$ ;  
 (ii)  $\text{CHPh}_2 \cdot \text{CMeBr} \cdot \text{COPh} + \text{KOH} = \text{CHPh}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{COPh} + \text{KBr}$ ;  
 but the formation of an unsaturated ketone is only observed when the bromo-ketone contains two aryl groups in the  $\beta$ -position. Klages, however, states (*Chem. Zeit.*, 1908, 33, 318) that phenyl vinyl ketone and its homologues are easily obtained by the action of potassium hydroxide on  $\alpha$ -bromo-ketones. The present author, however, finds that the substance described by Klages as phenyl vinyl ketone, b. p. 217—219°, is in reality a mixture of phenyl methyl diketone, b. p. 217—219°, phenyl ethyl ketone, b. p. 220—221°, and benzoyl-methylcarbinol, and that no unsaturated ketone can be detected among the products of this reaction, or of the action of potassium hydroxide on *p*-bromophenyl  $\alpha$ -bromoisobutyl ketone,



which substance, having a tertiary hydrogen atom in the  $\beta$ -position, might be expected to lose hydrogen bromide readily.

The formation of the diketone mentioned above is explained by the equation:  $2\text{R} \cdot \text{CO} \cdot \text{CHBrR}' + 2\text{KOH} = \text{R} \cdot \text{CO} \cdot \text{CO} \cdot \text{R}' + \text{R} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{R}' + 2\text{KBr} + \text{H}_2\text{O}$ .

*p*-Bromophenyl methyl diketone,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO} \cdot \text{COPh}$ , obtained by the action of potassium hydroxide on *p*-bromophenyl  $\alpha$ -bromoethyl ketone, is a yellow solid, m. p. 48°; the phenylhydrazone,  $\text{C}_{15}\text{H}_{13}\text{ON}_2\text{Br}$ , m. p. 199°, separates from alcohol in thin, yellow plates, and the dioxime,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_2\text{Br}$ , m. p. 237°, forms small, lustrous prisms from alcohol; it readily forms an additive compound with sodium hydrogen sulphite. *p*-Bromophenyl ethyl ketone and *p*-bromophenyl  $\alpha$ -hydroxy-ethyl ketone,  $\text{OH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ , are formed also in the above reaction; the latter is a pale yellow oil, b. p. 169°/15 mm., the acetyl derivative,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{Br}$ , of which forms a viscous, colourless liquid, b. p. 183—185°/16 mm.

*p*-Bromophenyl  $\alpha$ -bromoisobutyl ketone, when treated with potassium hydroxide, gave a yellow liquid, b. p. 168—169°/15 mm., which could not be proved to be a pure substance, and gave a dioxime,



m. p. 229°, fine needles from alcohol; the only other product of the reaction which was identified was *p*-bromophenyl isobutyl ketone,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ , m. p. 48°, which crystallises from methyl alcohol in large plates, and gives an oxime,  $\text{C}_{11}\text{H}_{14}\text{ONBr}$ , needles, m. p. 91—92°.

P. H.

**Nitroanthrone.** ARTHUR HANTZSCH and A. KORCZYŃSKI (*Ber.*, 1909, 42, 1216—1219).—The authors have succeeded in isolating a third modification of nitroanthrone, which is designated *nitro-anthranol*,  $\text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{NO}_2) \cdot \text{C}_6\text{H}_4$ . It is obtained as canary-yellow needles by rapidly cooling an ethereal solution of the red modification (*aci*-nitroanthrone) in the entire absence of moisture. Nitroanthranol

is extremely unstable, and changes rapidly into *aci*-nitroanthrone, which in turn passes into the colourless nitroanthrone.

*aci*-Nitroanthrone is most readily prepared by passing ammonia into an ethereal solution of nitroanthrone, subsequently treating the ammonium salt at  $-70^{\circ}$  with hydrogen chloride and evaporating the solution over solid potassium hydroxide (compare Meisenheimer and Connerade, Abstr., 1904, i, 391).

The absorption spectrum of nitroanthrone in chloroform is quite different from that of the sodium salt (sodium *aci*-nitroanthrone) in ethyl alcohol; the latter has two marked bands in the ultra-violet and one in the visible part of the spectrum; the former shows more or less general absorption.

The salts of *aci*-nitroanthrone, like those of the *aci*-nitrophenols, exist in red, yellow, and orange forms. The *ammonium* salt is red; the *potassium*, *rubidium*, *methylammonium*, and *dimethylammonium* salts are orange; the *benzylammonium* salt is yellow.

Attempts to prepare red *aci*-nitroanthrone ethers were unsuccessful.

W. H. G.

**Attempts to Prepare Methylcyclopentanetetrone.** OTTO DIELS and ALEX BÜCKING (*Ber.*, 1909, 42, 1576—1583. Compare Abstr., 1906, i, 438).—Alcoholic 1-methylcyclopentane-2:4:5-trione, ethyl nitrite, and a few drops of acetyl chloride react at  $0^{\circ}$  to form 3-oximino-

1-methylcyclopentane-2:4:5-trione,  $\begin{array}{c} \text{CHMe}\cdot\text{CO} \\ \text{CO}\text{---CO} \end{array} > \text{C:NOH}$ , which separates from hot water in pale yellow prisms, darkens at  $130^{\circ}$  and decomposes at  $172^{\circ}$  (corr.), readily absorbs  $1\frac{1}{2}$ —2 mols.  $\text{H}_2\text{O}$  from the air, forms an *oxime*,  $\text{C}_6\text{H}_8\text{O}_4\text{N}_2$ , which decomposes at  $164^{\circ}$  (corr.), and a salt with dimethylaniline,  $\text{C}_{14}\text{H}_{17}\text{O}_4\text{N}_2$ , m. p.  $124^{\circ}$  (decomp.), but does not react with phenylcarbimide, methyl sulphate, or diazomethane; the nitrogen cannot be eliminated without profound decomposition.

1-Methylcyclopentane-2:4:5-trione condenses readily with benzaldehyde, furfuraldehyde, and *p*-hydroxybenzaldehyde, the *furfurylidene* derivative,  $\text{C}_{11}\text{H}_8\text{O}_4$ , m. p.  $199^{\circ}$  (decomp.; corr.), crystallising in reddish-yellow prisms, but attempts to form ozonides from the condensation products, by the decomposition of which the tetrone might be produced, resulted only in complete decomposition.

*Dichloro-1-methylcyclopentane-2:4:5-trione*,  $\text{C}_6\text{H}_4\text{O}_3\text{Cl}_2$ , m. p.  $149^{\circ}$  (corr.), is formed by treating 1-methylcyclopentane-2:4:5-trione with a solution of chlorine in chloroform at  $0^{\circ}$ .

C. S.

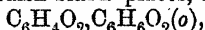
**Additive Compounds of Phenols and Quinones.** KURT H. MEYER (*Ber.*, 1909, 42, 1149—1153).—It is usually stated that a quinone (1 mol.) forms additive compounds with monohydric phenols (2 mols.) or dihydric phenols (1 mol.) (Jackson and Oenslager, Abstr., 1896, i, 293; Posner, *ibid.*, 1904, i, 1029). Siegmund (this vol., i, 109) describes an exception in the case of catechol, two molecules of which combine with one of benzoquinone. A number of additive compounds formed by the union of one molecule of a quinone with one of a monohydric phenol are described in the paper.

The author does not agree that these compounds are formed by the

aid of partial valencies of the atoms, but regards them as true additive compounds, formed by the addition of the phenol molecules to the oxygen atoms of the quinones (compare Abstr., 1908, i, 731).

Benzophenone forms the following compounds:  $C_6H_4O_2 \cdot C_6H_4Cl \cdot OH$ , orange-yellow needles, m. p.  $85^\circ$ ;  $C_6H_4O_2 \cdot 2C_6H_4Cl \cdot OH$ , dark brown needles, m. p.  $72^\circ$ ;  $C_6H_4O_2 \cdot C_6H_4Br \cdot OH$ , orange-red needles, m. p.  $77^\circ$ ;  $C_6H_4O_2 \cdot 2C_6H_4Br \cdot OH$ , dark reddish-brown needles, m. p.  $62^\circ$ . The compounds with two molecules of phenol are relatively unstable, and when warmed with light petroleum readily yield the compounds containing one molecule of the phenol.

$C_6H_4O_2 \cdot C_{10}H_7 \cdot OH(a)$ , dark red plates, m. p.  $100^\circ$  (decomp.);  $C_6H_4O_2 \cdot 2C_{10}H_7 \cdot OH$ , dark red needles, m. p.  $120^\circ$  (decomp.);  $C_6H_4O_2 \cdot C_{10}H_7 \cdot OH(\beta)$ , reddish-black plates, m. p.  $85^\circ$ ;



long, dark green or, in reflected light, red needles, m. p.  $100-150^\circ$ .

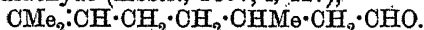
Compound with  $\alpha$ -naphthaquinone,  $C_{10}H_6O_2 \cdot C_{10}H_7 \cdot OH(a)$ , red needles, m. p.  $97^\circ$ .

Compound with phenanthraquinone,  $C_{10}H_6O_2 \cdot C_{10}H_7 \cdot OH(a)$ , red plates, m. p.  $139^\circ$ .

Most of the compounds were prepared by crystallising mixtures of the components from light petroleum, and in most cases an excess of one of the components was necessary. The compounds are unstable, and are decomposed to a large extent in solution. J. J. S.

**Chemical Action of Light.** GIACOMO L. CIAMICIAN and PAUL SILBER (*Ann. Chim. Phys.*, 1909, [viii], 16, 474—520. Compare Abstr., 1901, i, 329, 390, 547; 1902, i, 433; 1903, i, 39, 171, 562; 1904, i, 161; 1905, i, 335, 414; 1906, i, 10; 1907, i, 19, 119, 484).—A detailed account of work already published (compare Abstr., 1907, i, 587; 1908, i, 277, 555). M. A. W.

**Chemical Action of Light. XIV.** GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 317—322; *Ber.*, 1909, 42, 1510—1515).—The authors have shown previously that, in aqueous-alcoholic solution, menthone is decomposed in two ways by the action of light, yielding decoic acid and an aldehyde (Abstr., 1907, i, 587), the latter being regarded as probably identical with Wallach's menthocytronellaldehyde (Abstr., 1897, i, 427),



They now find, however, that the acid  $C_{10}H_{18}O_2$ , corresponding with this aldehyde, has b. p.  $252-253^\circ$ , whilst Wallach's menthonenic acid (*loc. cit.*), corresponding with menthocytronellaldehyde, has b. p.  $257-261^\circ$ . On oxidation, firstly with alkaline permanganate and then with chromic acid, the acid b. p.  $252-253^\circ$  yields isobutyric and  $\beta$ -methylglutaric acids, so that the corresponding aldehyde is probably not identical with Wallach's citronellaldehyde, but has the constitution  $CHMe_2 \cdot CH \cdot CH \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CHO$ . There is a possibility, however, of the double bond being displaced by the action of alkaline permanganate (compare Harries and Schauwecker, Abstr., 1901, i, 730; Perkin and Wallach, this vol., i, 154).

When exposed to the air, menthone undergoes oxidation to the

ketonic acid,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared by Arth (Abstr., 1886, 892) and by Beckmann and Mehrländer (Abstr., 1896, i, 312) by oxidising menthol with chromic acid, and obtained in the form of the oxime by Baeyer and Manasse (Abstr., 1894, i, 522) by treating menthone with amyl nitrite and hydrochloric acid and hydrolysing the nitrosomenthone thus formed (compare also Baeyer and Oehler, Abstr., 1896, i, 247). It is probable that the conversion of menthone to the ketonic acid proceeds by way of an intermediate hydroxy-acid,  $\text{CHMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ ; this view is supported by the observation that the crude ketonic acid, after distillation, was not completely soluble in sodium carbonate, but left a residue having the characteristic odour of lactones.

It will be seen that the action of light on organic compounds may lead to different results, according as oxygen is present or absent. A similar fact was observed in the case of stilbene (Abstr., 1903, i, 171; 1904, i, 161), and also with the yellow and white  $\alpha\beta$ -diphenyl- $\Delta^{\alpha\gamma\epsilon\eta}$ -octatetrenes (this vol., i, 219).

T. H. P.

**Dynamic Isomerism.** HENRY E. ARMSTRONG, THOMAS M. LOWRY, SYDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Brit. Assoc. Report*, 1908, 112—115).—This report deals with the use of carbonyl chloride as an agent for arresting isomeric change (compare Lowry and Magson, *Trans.*, 1908, 93, 119—132), and with the relationship between absorption spectra and isomeric change with halogen, nitro- and sulpho-derivatives of camphor.

T. H. P.

**Compounds of Ketones and Aldehydes with Acids.** ALEXIS A. SHUKOFF and F. S. KASATKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 157—166).—The authors have investigated the compounds formed by camphor with nitric, phosphoric, hydrochloric, hydriodic, and nitrous acids, by benzophenone and benzaldehyde with nitric acid, and by heptaldehyde and methyl nonyl ketone with phosphoric acid (compare Baeyer and Villiger, Abstr., 1901, i, 658; Archibald and McIntosh, *Trans.*, 1904, 85, 919; McIntosh, *Trans.*, 1905, 87, 784).

The interaction of recrystallised camphor (1 mol.) and nearly anhydrous nitric acid (1 mol.) yields an almost colourless, viscid liquid, which dissolves readily in the organic solvents and gradually solidifies to long, acicular crystals,  $\text{C}_{10}\text{H}_{16}\text{O} \cdot \text{HNO}_3$ , m. p.  $24^\circ$ . The freezing-point curve for mixtures of camphor and nitric acid exhibits two maxima, indicating the existence of the two compounds: (1)  $\text{C}_{10}\text{H}_{16}\text{O} \cdot \text{HNO}_3$ , solidifying at  $24.2^\circ$ , and (2)  $(\text{C}_{10}\text{H}_{16}\text{O})_2 \cdot \text{HNO}_3$ , solidifying at  $2.2^\circ$ . The latter compound separates when a mixture of the two substances containing  $32.6$ — $44.6$  mols. per cent. of acid is crystallised from light petroleum.

Camphor and phosphoric acid yield the compound,  $\text{C}_{10}\text{H}_{16}\text{O} \cdot \text{H}_3\text{PO}_4$ , which solidifies in short, colourless crystals, m. p. about  $29^\circ$ . This compound corresponds with the only maximum of the freezing-point curve, which exhibits two minima answering to the eutectics of this compound in camphor and phosphoric acid.

Camphor and hydriodic acid give the compound  $C_{10}H_{16}O, HI$ , m. p. 29—30° (compare Fleischer and Kékulé, Abstr., 1873, 1228).

On passing dry hydrogen chloride into a vessel containing powdered camphor, a liquid is obtained, which absorbs moisture from the air, decomposes into its constituents, and solidifies at -4.2° to a colourless, crystalline mass.

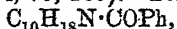
Similarly, dry nitrous anhydride and camphor yield an almost colourless, transparent liquid, which does not solidify at -35°.

Benzophenone and nitric acid in molecular proportions yield the compound,  $CPh_2O, HNO_3$ , m. p. 39°, which can be recrystallised from ether. The existence of this compound is interesting, since, according to Claisen (Abstr., 1896, i, 464; 1898, i, 421) and Baeyer (Abstr., 1901, i, 658), benzophenone should not give double compounds with acids.

Benzaldehyde and nitric acid give the compound,  $C_7H_6O, HNO_3$ , m. p. +5.4°.

In the case of heptaldehyde and methyl nonyl ketone with phosphoric acid, compounds solidifying at +12° and +3° respectively were obtained, but their compositions were not determined. T. H. P.

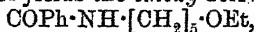
**Decomposition of Camphidine by means of Phosphorus Pentachloride, and New Derivatives of  $\epsilon$ -Chlorobenzoylamylamine.** JULIUS VON BRAUN (*Ber.*, 1909, 42, 1429—1436. Compare Abstr., 1905, i, 596; 1907, i, 79, 105).—*Benzoylcamphidine*,



distils, at 217—220°/11 mm., and sets to a crystalline mass, m. p. 61°. When its chloroform solution is warmed gently with phosphorus pentachloride or pentabromide, the corresponding halogenated amides,  $-NCX_2Ph$ , are formed, and are precipitated as hygroscopic masses on the addition of light petroleum. The halogen is immediately replaced by oxygen in the presence of water.

The chlorinated *amide*,  $C_{10}H_{18}Cl \cdot NH \cdot CPh$ , can be obtained by treating benzoylcamphidine with the pentachloride under certain well-defined conditions. It crystallises from alcohol in long, slender needles, m. p. 113°, and has  $[\alpha]_D^{25} + 32.4^\circ$  in benzene solution. This compound is extremely stable; it can be heated to a temperature considerably above its m. p., or can be boiled with alkalis without losing benzoic acid or hydrogen chloride, and does not react with nascent hydrogen or potassium cyanide; but when heated at 110—120° for several hours with fuming hydrochloric acid, a small amount of benzoic acid is formed. Boiling with sodium methoxide or sodium ethoxide solutions regenerates the original benzoylcamphidine.

$\epsilon$ -Chlorobenzoylamylamine (Abstr., 1905, i, 596) is also stable towards reducing agents, but when boiled with a solution of sodium ethoxide in ethyl alcohol yields the *ethoxy*-derivative.



b. p. 225—228°/14 mm. The *methoxy*-compound,  $C_{12}H_{19}O_2N$ , has b. p. 219—222°/12 mm. Both compounds are stable towards alkaline hydrolysing agents, but are decomposed by hydrochloric acid at high

temperatures. Distillation with phosphorus pentachloride gives rise to benzonitrile and methoxy- or ethoxy-chloroamylenes.

*Benzoylphthalylcadaverine*,  $\text{COPh}\cdot\text{NH}\cdot[\text{CH}_2]_{15}\cdot\text{N}\cdot\text{C}_2\text{O}_2\cdot\text{C}_6\text{H}_4$ , obtained by the action of potassium phthalimide on  $\epsilon$ -chlorobenzoylamylamine, crystallises from hot alcohol in felted needles, m. p.  $126^\circ$ . When heated at  $125^\circ$  with hydrochloric acid, it yields both benzoic and phthalic acids, but the former in smaller quantity, so that the phthalyl group appears to be removed more easily than the benzoyl. The dibenzoyl and diphtalyl compounds are both more resistant than the mixed diacyl derivative towards hydrochloric acid. J. J. S.

**The Terpene and Camphor Series. V. Structure of Guaïol.** A. L. GANDURIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 288—298. Compare Tschugaeff, Abstr., 1908, i, 93).—The author has investigated guaïol and its derivatives (compare Wallach and Tuttle, Abstr., 1894, i, 538), his results indicating that this substance is a dicyclic, monohydric, tertiary alcohol,  $\text{C}_{15}\text{H}_{25}\cdot\text{OH}$ , the molecule of which contains one ethylene linking.

The esterification constant of guaïol with acetic anhydride gradually falls in magnitude, the mean value being 0.00068, which, together with the irregular course of the esterification, indicates that the alcohol is a tertiary one. This conclusion is confirmed by the behaviour of guaïol when heated with zinc dust (compare Semmler, Abstr., 1894, i, 611), under which conditions it yields *dihydroguaïene*,  $\text{C}_{15}\text{H}_{26}$ , a colourless liquid, b. p.  $122^\circ/11$  mm.,  $[\alpha]_D^{25} - 26.65^\circ$ ,  $D_4^{25} 0.9089$ ,  $D_4^{25} 0.8914$ ,  $n_D^{25} 1.49317$ .

*Guaïol methyl ether*,  $\text{C}_{15}\text{H}_{25}\cdot\text{OMe}$ , is a faintly yellow liquid, b. p.  $141\text{—}143^\circ/9$  mm.,  $[\alpha]_D^{20} - 31.81^\circ$ ,  $D_4^{25} 0.9513$ ,  $D_4^{25} 0.9332$ ,  $n_D^{18.5} 1.48963$ . The value of the molecular refraction indicates that this compound, and hence also guaïol itself, is a dicyclic compound with one ethylene linking.

*Guaïene* (compare Wallach and Tuttle, Abstr., 1894, i, 438),  $\text{C}_{15}\text{H}_{24}$ , is a colourless liquid, b. p.  $124^\circ/11$  mm.,  $[\alpha]_D^{25} - 66.11^\circ$ ,  $D_4^{25} 0.9133$ ,  $D_4^{25} 0.8954$ ,  $n_D^{25} 1.49468$ ; the molecular refraction, 66.46, is in agreement with the theoretical number (66.28) for a dicyclic hydrocarbon containing two ethylene linkings. T. H. P.

**Crystals of Juniperol.** H. RAMSAY (*Zeitsch. Kryst. Min.*, 1909, 46, 281—282).—Juniperol,  $\text{C}_{15}\text{H}_{24}\text{O}$ , the sesquiterpene alcohol from oil of juniper bark, is triclinic  $[a:b:c = 0.7243:1:0.7574; a = 90^\circ 14', \beta = 103^\circ 30', \gamma = 90^\circ 5']$ . L. J. S.

**Terpenes and Ethereal Oils. XCVIII. Transformation of Pulegone into isoPulegone during Oximation in Alkaline Solution.** OTTO WALLACH [with ADOLF ROSENBAUGH and RUDOLF MÜLLER] (*Annalen*, 1909, 365, 240—254. Compare Abstr., 1908, i, 997).—It would appear from the results of recent work on the reduction of 1:2-unsaturated compounds that pulegoneoxime should yield menthylamine when reduced. The oxime derived from pulegone yields, however, a crystalline base,  $\text{C}_{10}\text{H}_{17}\cdot\text{NH}_2$  (compare Wallach, Abstr., 1894, i, 46; 1896, i, 309), from which it seems probable that

f f 2

the oxime is really *isopulegoneoxime*. The m. p.'s for the latter substance recorded by various investigators are, however, extremely divergent (compare Tiemann and Schmidt, *Abstr.*, 1897, i, 198; Barbier and Léser, *Abstr.*, 1897, i, 537; Harries and Roeder, *Abstr.*, 1900, i, 182; Semmler, *Abstr.*, 1905, i, 222). The author has therefore repeated his experiments on the direct formation of an oxime from pulegone. It is found that pulegone in the presence of alkali and hydroxylamine rapidly changes into *isopulegone*, and that the oxime formed is *isopulegoneoxime*. In the preparation of the oxime a certain proportion of the pulegone is hydrolysed by the alkali, as a result of which acetoxime and *cyclomethylhexanoneoxime* are also formed.

*isoPulegoneoxime* has m. p. 120—121°,  $[\alpha]_D^{25} - 25.833^\circ$  in methyl alcohol. In agreement with the observation made previously (*loc. cit.*), it yields pulegone when decomposed by sulphuric acid; when decomposed by oxalic acid, however, it yields *isopulegone*. The base produced by reducing the oxime forms a *hydrochloride*,  $C_{10}H_{19}N \cdot HCl$ , obtained as a white powder, and is converted by nitrous acid into *isopulegol*.

It is shown definitely that the oxime derived directly from pulegone is identical with the oxime of *isopulegone* prepared from pulegone hydrobromide by treatment with lead nitrate. In agreement with the statement of Tiemann and Schmidt (*loc. cit.*), two oximes are obtained from *isopulegone* prepared from citronellaldehyde; *isopulegone* prepared in this way is shown to be a mixture of active and inactive ketones, yielding in consequence active *isopulegoneoxime*, m. p. 120—121°, and inactive *isopulegoneoxime*, m. p. 138—139°. The fact that Harries (*loc. cit.*) obtained an oxime, m. p. 143°, shows that by his method of preparation an oxime free from active components is formed.

W. H. G.

**New Method of Isomerisation in the Terpene Series.** GÉZA AUSTERWEIL (*Compt. rend.*, 1909, 148, 1197—1199).—An 18% yield of a bornyl ester is obtained when pinene is heated to a moderate temperature in an autoclave with an organic acid. When the pressure is increased by connecting the autoclave to a bottle of liquid carbon dioxide, and the heating is continued for several hours at 200°, the yield is considerably increased. The limonene formed simultaneously is separated by steam distillation. The borneol obtained by hydrolysis of the ester is optically active.

W. O. W.

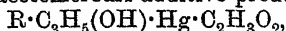
**Caryophyllene.** CARL W. HAARMANN (*Ber.*, 1909, 42, 1062—1067. Compare Deussen, this vol., i, 171).—Caryophyllene, when oxidised with permanganate equivalent to 8 atoms of oxygen, forms a *glycol*,  $C_{14}H_{22}O_4$ , m. p. 120°, b. p. 210°/10 mm., identical with that described by Deussen (*loc. cit.*). It forms an *oxime*, m. p. 188.5°, and when heated with 1% sulphuric acid is converted into a *compound*,  $C_{14}H_{20}O_3$ , b. p. 193°/20 mm., which does not form an oxime. When further oxidised with chromic acid, the glycol is converted into an *aldehyde*,  $C_{14}H_{20}O_4$ , m. p. 156—157°, which forms a *monophenylhydrazone*, m. p. 167°. On further oxidation of the glycol with permanganate at room temperature, an *acid*,  $C_{14}H_{20}O_5$ , m. p. 171° (decomp.), is obtained. This forms

a sparingly soluble *sodium* salt, but is not a lactonic acid. When oxidised at 50°, an *acid*, m. p. 201—202°, and an *acid*, m. p. 162°, are obtained.

Further products obtained on oxidation of caryophyllene are an *acid*,  $C_{10}H_{16}O_3$  (compare Deussen, *loc. cit.*), b. p. 195—197°/23 mm., and a *compound*,  $C_{11}H_{18}O_3$ , m. p. 122°, which is stable towards permanganate. On oxidation of caryophyllene at 100°, *αα*-dimethylsuccinic acid is formed. When oxidised with ozone, an ozonide,  $C_{15}H_{22}O_7$ , is formed.

E. F. A.

**Separation of Allyl and Propenyl Compounds in Ethereal Oils.** LUIGI BALBINO (*Ber.*, 1909, 42, 1502—1506. *Atti R. Accad. Lincei*, 1909, [v], 18, i, 372—376. Compare *Abstr.*, 1906, i, 186).—When treated with cold saturated aqueous mercuric acetate, allyl compounds form the acetomercuri-additive product,



whereas propenyl compounds give rise to the corresponding glycols, the mercuric acetate being reduced to mercurous compounds or to mercury. It is now found that when a definite quantity of mercuric acetate is added to a mixture of propenyl and allyl compounds, only the acetomercuri-derivative of the allyl compound is formed, and the propenyl derivative remains unaltered. It can be isolated by extraction with ether or steam distillation. Subsequently, the acetomercuri-compound may be reduced by means of zinc and sodium hydroxide, and the allyl compound recovered by steam distillation. The method has been applied to the separation of anethole and chavicol methyl ether, of safrole and *isosafole* of myristicin and *isomyristicin*, and lastly of *apiole* and *isoapiole*.

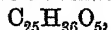
E. F. A.

**Composition of the Oil of an African Balsam.** HUGO VON SODEN (*Chem. Zeit.*, 1909, 33, 428).—An African balsam yielded on distillation in steam about 45% of a volatile oil, which on being subjected to the usual tests, such as treatment with hydrogen chloride in ethereal solution, etc., proved to be composed mainly of *d*-cadinine. The investigation is, however, being continued.

L. DE K.

**American Colophony. I. Resin of the Norway Pine.** GEORGE B. FRANKFORTER (*J. Amer. Chem. Soc.*, 1909, 31, 561—565).—Previous work on the investigation of resins is reviewed, and the conclusion is drawn that every resin contains at least one distinct and characteristic acid in addition to abietic acid or one of its isomerides.

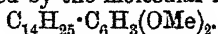
A sample of oleo-resin obtained from the Norway pine (*Pinus resinosa*) was a colourless, mobile liquid, which had  $D_4^{20}$  0.8137,  $[\alpha]_D^{20} + 4^\circ$ ,  $n_D^{20}$  1.4788. After removing the terpenes, which constituted about 20% of the whole, a nearly white, brittle resin, m. p. 81—85°, remained. This resin, on fractional precipitation from its solution in ether or alcohol, yielded a mixture of resinic and abietic acids, which were separated by means of their ammonium salts. *Resinic acid*,



m. p. 97—98°, forms a white, crystalline powder; its *ammonium* and *barium* salts are described. The abietic acid melted at 129—130°.

E. G.

**Main Constituent of Japanese Lac.** URUSHIOL and Urushiol Dimethyl Ether. RIKŌ MAJIMA (*Ber.*, 1909, 42, 1418—1423. Compare Abstr., 1907, i, 1032).—By distilling in a high vacuum, the so-called "urushic acid" is separated from accompanying substances of high molecular complexity, and is found to contain two hydroxyl groups, but no carboxyl group, and, for this reason, the name *urushiol* is proposed as better representing its nature. Urushiol is a viscid, brown oil having  $D_4^{25}$  0.9687; it reduces ammoniacal silver nitrate solution, and otherwise behaves like the raw material; it is vigorously attacked by nitric acid, D 1.2, and also by bromine. It does not contain nitrogen, and, from combustions and molecular-weight determinations, it is considered to have the molecular formula  $C_{20}H_{30}O_2$ . Besides yielding a dimethyl ether and a diacetyl compound, it behaves in general as a dihydroxyphenol. When purified urushiol is boiled with sodium ethoxide and methyl iodide in an atmosphere of hydrogen, a somewhat crude methylated product is obtained as an oil. Purified by fractional distillation, it was obtained as a colourless oil, having b. p. 190—195° and  $D_4^{25}$  0.9419, and, according to results of analysis, molecular-weight determinations, and molecular dispersions, is probably to be represented by the molecular formula



It is considered probable that the non-volatile portion obtained from fractionating the purified urushiol consists chiefly of highly polymerised urushiol.

J. V. E.

**Crystalline Chlorophylls.** ARMAND GAUTIER (*Bull. Soc. chim.*, 1909, [iv], 5, 319—320).—In connexion with the publication of the paper by Willstätter and Benz (Abstr., 1908, i, 199), the author points out that he first prepared chlorophyll in a crystalline condition, and established certain facts regarding its composition, etc., which have since been confirmed (Abstr., 1880, 266).

T. A. H.

**Bilirubin.** MAURICE PIETTE (*Compt. rend.*, 1909, 148, 1213—1215).—A new colouring matter, to which the name *biliflavin* is given, has been isolated from biliary calculi of oxen. This resembles bilirubin, and occurs in small, yellow crystals containing 9.7% nitrogen. Hydrolysis of bilirubin and biliflavin leads to the production of a colourless substance, having the characters of a higher fatty acid, and containing 71.85—72.19% carbon and 12.5—12.62% hydrogen.

Attention is drawn to the intimate connexion existing between hæmatin and the pigments of the bile (compare Abstr., 1906, i, 55).

W. O. W.

**Constitution of Tannin.** V. MAXIMILIAN NIERENSTEIN (*Ber.*, 1909, 42, 1122—1126. Compare Abstr., 1908, i, 897).—Penta-acetyl-leucotannin, obtained by the reduction of penta-acetyltannin or prepared from the leucotannin present in tannin, is hydrolysed by boiling dilute sulphuric acid, yielding gallic acid and gallaldehyde, and, when dissolved in 40% acetic acid, is oxidised by boiling dilute sulphuric acid and potassium persulphate, forming, together with a small quantity of ellagic acid, a red powder, to which the name *purpurotannin* is given.

Purpurotannin yields naphthalene when distilled with zinc dust. Penta-acetyl-leucotannin forms trihydroxyglutáric acid when oxidised with potassium permanganate and dilute sulphuric acid. C. S.

**Tannin from the Bark of Eucalyptus Occidentalis.** J. DEKKER (*Arch. Néerland*, 1909, ii, 14, 50—80).—The tannin precipitated by ether from the alcoholic extract of the bark of *Eucalyptus occidentalis* (*maletto-bark*) has the empirical formula  $(C_{19}H_{20}O_9)_n$  [Strauss and Gschwendner, *Abstr.*, 1906, i, 596, give  $(C_{43}H_{50}O_{20})_2$ ]; on heating with acetic anhydride and sodium acetate it loses water and yields the *acetyl* derivative,  $C_{38}H_{28}O_{17}Ac_{10}$ , and on benzoylation in alkaline solution it undergoes oxidation and forms the *benzoyl* derivative,  $C_{19}H_{25}O_{12}Bz_5$ ; when heated with zinc dust and a 15% solution of sodium hydroxide, the tannin yields small quantities of gallic acid and phloroglucinol, whilst on dry distillation it yields pyrogallol and traces of other phenols.

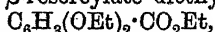
When the *maletto* tannin is boiled with dilute sulphuric acid, no sugar is formed, but the substance loses water and yields the sparingly soluble red compound (*maletto-red*),  $C_{57}H_{50}O_{22}$ , which forms an *acetyl* derivative,  $C_{57}H_{35}O_{20}Ac_{15}$ . M. A. W.

[Completely Methylated Flavone Derivatives.] JOSEF HERZIG and BR. HOFMANN (*Ber.*, 1909, 42, 1424. Compare this vol., i, 165).—A reply to Waliaschko (this vol., i, 248) on the preparation of trimethyl- and pentamethyl-quercetin. J. V. E.

**Synthesis of Xanthophanic Acid: 7-Hydroxychromone-6-carboxylic Acid.** V. CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1909, 42, 1392—1405. Compare *Abstr.*, 1908, i, 548).—The authors' experiments in the direction of synthesising xanthophanic acid have led to the synthesis of 7-hydroxychromone-6-carboxylic acid, from which they hope to obtain xanthophanic acid.

Condensation of ethyl resacetophenonecarboxylate with ethyl ethoxymethyleneacetoacetate in presence of a small proportion of sodium ethoxide in alcoholic solution (*loc. cit.*) leads to the formation of an *ester*,  $CO_2Et \cdot C_6H_2(OH) \begin{smallmatrix} O-C \cdot CAc \cdot CH \cdot OH \\ || \\ CO \cdot CH \end{smallmatrix}$  (?), which crystallises from a mixture of benzene and light petroleum in almost colourless, silky needles, m. p. 163—165°. When hydrolysed with potassium hydroxide, this ester yields an *acid*,  $C_{14}H_{10}O_7$  (?), crystallising from acetic acid in almost colourless needles, m. p. 201—203° (decomp.); the *barium*,  $(C_{14}H_9O_7)_2Ba$ , and *copper* salts were analysed. As these compounds are not closely related to xanthophanic acid, they were not investigated further.

Starting from  $\beta$ -resorcylic acid, the action of silver oxide and ethyl iodide yields ethyl  $\beta$ -resorcyate diethyl ether,

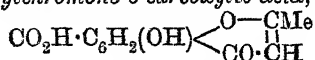


as a faintly brown oil, and this is converted into  $\beta$ -resorcylic acid diethyl ether by alcoholic potassium hydroxide solution. The mixture of resacetophenonecarboxylic acid mono- and di-ethyl ethers obtained by treating  $\beta$ -resorcylic acid diethyl ether with acetyl chloride and

aluminium chlorides (Abstr., 1908, i, 548) is then treated with silver oxide and ethyl iodide, by which means it is converted into *ethyl resacetophenonecarboxylate diethyl ether*,  $C_6H_5Ac(OEt)_2 \cdot CO_2Et$ , which crystallises from light petroleum in slender, white needles, m. p. 95—97°, and on heating with concentrated hydriodic acid loses all its ethyl groups, yielding resacetophenonecarboxylic acid.

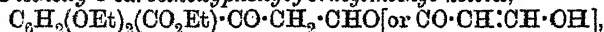
Condensation of ethyl resacetophenonecarboxylate diethyl ether with ethyl acetate in presence of sodium yields *ethyl 2:4-diethoxybenzoylacetone-5-carboxylate*,  $CO_2Et \cdot C_6H_3(OEt)_2 \cdot CO \cdot CH_2Ac$ , which crystallises from alcohol in greenish-yellow leaflets, m. p. 138—140°, and gives with sulphuric acid an orange-yellow solution showing green fluorescence.

*7-Hydroxy-2-methylchromone-6-carboxylic acid*,

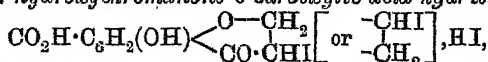


(compare Bloch and von Kostanecki, Abstr., 1900, i, 308), obtained by treating ethyl 2:4-diethoxybenzoylacetone-5-carboxylate with fuming hydriodic acid, separates in colourless, silky needles, m. p. 301° (decomp.), and in alcoholic solution gives a reddish-brown coloration with ferric chloride; its solutions in alkali hydroxide or carbonate show bluish-green, and those in concentrated sulphuric acid, bright green, fluorescence.

*2:4-Diethoxy-5-carbethoxyphenyl formylmethyl ketone*,



obtained by the condensation of ethyl resacetophenonecarboxylate diethyl ether with ethyl formate in presence of sodium, crystallises from light petroleum in shining, colourless needles, m. p. 116—117°, and, when treated with alkali, is either saponified or resolved into the  $\beta$ -diketone. When this compound is melted with half its weight of ethyl acetate in a water-bath, and a few bubbles of hydrogen chloride are passed into the cooled paste, a beautiful red coloration, changing to brown, is obtained, the crystalline compound formed being under investigation. When this compound is heated with a glacial acetic acid solution of hydrogen iodide, it is converted into 2[or 3]-*iodo-7-hydroxychromanone-6-carboxylic acid hydriodide*,



which separates in faintly yellow, shining needles, m. p. 217° (decomp.), and loses its hydrogen iodide when treated with sulphuric acid, giving the carboxylic acid, which crystallises from acetic acid as the *acetate*,  $C_{10}H_7O_5I, C_2H_4O_2$ , decomposing at 270—280°.

*7-Hydroxychromone-6-carboxylic acid*,  $CO_2H \cdot C_6H_2(OH) < \begin{array}{c} O-CH \\ || \\ CO \cdot CH \end{array}$ ,

obtained by the action of 2% potassium hydroxide solution on 2(or 3)-*iodo-7-hydroxychromanone-6-carboxylic acid hydriodide*, separates as an almost white, crystalline powder, m. p. 297° (decomp.), gives a red coloration with ferric chloride in alcoholic solution, and forms yellow solutions with faint green fluorescence with alkali hydroxide or carbonate, and a yellow, non-fluorescent solution with concentrated sulphuric acid.

When heated with an acetic acid solution of hydrogen iodide in a sealed tube, 2:4-diethoxy-5-carbethoxyphenyl formylmethyl ketone yields an acid colouring matter,  $C_{20}H_{14}O_8$  (?), which separates in orange-red, crystalline flocks, and seems to retain the chromone group, since it gives a fluorescent solution in concentrated sulphuric acid.

T. H. P.

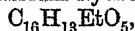
**Glaucophanic and Xanthophanic Acids. VI.** CARL LIEBERMANN and H. TRUCHSÄSS (*Ber.*, 1909, 42, 1405—1412).—From the too high yields of "transformation products" yielded by the glaucophanic acids, the authors concluded that the formula  $C_{27}H_{26}O_{13}$ , ascribed by Claisen (*Abstr.*, 1897, i, 594) to ethylglaucophanic acid, is not quite accurate (*Abstr.*, 1907, i, 890).

The authors have attempted to settle the composition of this acid by analysis, but the results of their work render it only more probable that the formula is  $C_{25}H_{24}O_{11}$ , rather than  $C_{27}H_{26}O_{13}$ .

Ethylglaucophanic acid forms a number of sparingly soluble salts, which do not lend themselves to the ordinary methods of molecular-weight determination. The following salts have been prepared and analysed: *p*-Bromoaniline,  $C_{25}H_{24}O_{11}, C_6H_6NBr$ ; *p*-iodoaniline,  $C_{25}H_{24}O_{11}, C_6H_6NI$ ; pyridine,  $C_{25}H_{24}O_{11}, C_5H_5N$ ; *p*-bromoquinoline,  $C_{25}H_{24}O_{11}, C_9H_6NBr$ ; *p*-iodoquinoline,  $C_{25}H_{24}O_{11}, C_9H_6NI$ ; rubidium,  $C_{25}H_{23}O_{11}Rb$ , and caesium.

Taking the formula  $C_{25}H_{24}O_{11}$  as correct, the molecule contains two methyl groups, and the formula of methylglaucophanic acid must be  $C_{23}H_{20}O_{11}$ .

The by-products from ethyl- ( $C_{20}H_{22}O_5$ ) and methyl-glaucophanic acids ( $C_{18}H_{18}O_5$ ) contain in each case two alkyl groups, and the de-alkylated residue after estimation of the alkoxy-groups (compare *Abstr.*, 1906, i, 556) has the composition  $C_{16}H_{14}O_5$ , crystallises from acetic acid in stable, colourless needles, m. p. 274°, and exhibits the behaviour of an acid ester; it functions as a dibasic acid, and, on hydrolysis with alcoholic potassium hydroxide, yields the ester,



m. p. 212—214°. Both the "by-products" yield hydrazones; that from the ethyl "by-product,"  $C_{20}H_{24}O_4N_2$ , crystallising from a mixture of benzene and light petroleum in white flocks, m. p. 127°, and that from the methyl "by-product" having m. p. 141—142°. As these "by-products" contain two carbethoxy- (or carbmethoxy-) groups and one keto-group, the chemical functions of all the oxygen atoms are accounted for.

T. H. P.

**Thiosalicyclic [*o*-Thiolbenzoic] Acid and Thioxanthone.** FRITZ MAYER (*Ber.*, 1909, 42, 1132—1137).—The paper gives merely an account of some derivatives of thiosalicyclic acid. The acid and acetic anhydride when heated at 140° for six hours yield phenyl disulphide and thioxanthone,  $C_6H_4 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} C_6H_4$ , m. p. 209°, which forms yellow crystals and gives a fluorescent, green solution in concentrated sulphuric acid. The same two products are obtained by the distillation of phenyl-

*thiosalicylate* (*thiosalol*),  $\text{SH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Ph}$ , m. p.  $91^\circ$ , which is obtained from phenol, thiosalicylic acid, and phosphoryl chloride at  $135^\circ$ . By heating bromobenzene, methyl thiosalicylate, copper powder, and alcoholic sodium methoxide with a little xylene for four hours at  $160^\circ$ , distilling the product with steam, boiling the residue with sodium hydroxide, and acidifying the alkaline solution, *o*-phenylthiolbenzoic acid is obtained, which is readily converted into thioxanthone by concentrated sulphuric acid. Thioxanthone, suspended in an alcoholic solution of potassium ethoxide, is boiled with zinc dust, whereby thioxanthidrol is formed, which is changed to thioxanthone by heating at  $160$ — $170^\circ$  with glycerol (1 part) and 15 parts of sulphuric acid ( $62^\circ$  B $\acute{e}$ ). Xanthidrol under similar conditions yields xanthone.

When thioxanthone, dissolved in hot glacial acetic acid, is treated with zinc dust and subsequently with hydrochloric acid, *dithioxanthylene*,  $\text{S} \langle \text{C}_6\text{H}_4 \rangle \text{C} : \text{C} \langle \text{C}_6\text{H}_4 \rangle \text{S}$ , m. p.  $346^\circ$ , is obtained, which crystallises from nitrobenzene in pale yellow needles. C. S.

**Thianthren [Diphenylene Disulphide].** KARL FRIES and W. VOLK (*Ber.*; 1909, 42, 1170—1176).—Thiophenols react with concentrated sulphuric acid, yielding disulphides (Stenhouse, *Annalen*, 1869, 149, 250), but these in their turn dissolve in the concentrated acid, yielding characteristic blue- or violet-coloured solutions, from which water precipitates colourless compounds. The second reaction is one of oxidation, as sulphur dioxide is evolved copiously during the process of solution. Thianthren derivatives have been isolated from the precipitates, and the blue or violet colour of the sulphuric acid solutions are due to these compounds.

Thianthren, 3:7-dimethylthianthren, naphthathianthren, and 2:4:6:8-tetrachloro-3:7-dihydroxythianthren have been obtained in this way from thiophenol, thio-*p*-cresol, thio- $\beta$ -naphthol, and dichlorothioquinol respectively. Other colourless products are formed at the same time, but so far these have not been investigated. The yield of thianthren derivatives usually varies from 10—20%, but in the case of thio-*p*-cresol reaches 50%. The disulphides are undoubtedly first oxidised to disulphoxides, since the latter yield the thianthren derivatives more readily than the disulphides.

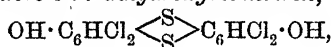
The thianthrens give coloured compounds with sulphuric, nitric, and trichloroacetic acids, and also with aluminium chloride, antimony pentachloride, ferric chloride, and stannic chloride.

3:7-Dimethylthianthren crystallises from glacial acetic acid in long, colourless, compact needles, m. p.  $123^\circ$ . Jacobson and Ney (*Abstr.*, 1889, 772) give  $116^\circ$ , and Krafft and Lyons (*ibid.*, 1896, i, 297) give  $117$ — $118^\circ$ . With ferric chloride it yields compact crystals of the compound,  $\text{C}_{14}\text{H}_{12}\text{S}_2 \cdot \text{FeCl}_3$ , which has a bluish-black lustre. 3:7-Dimethylthianthrene monoxide,  $\text{C}_6\text{H}_3\text{Me} \langle \text{SO} \rangle \text{C}_6\text{H}_3\text{Me}$ , obtained by the action of dilute nitric acid (D 1.2) on dimethylthianthren, crystallises from methyl alcohol in quadratic prisms, m. p.  $94^\circ$ . It dissolves in concentrated sulphuric acid, yielding a violet-coloured solution,

which gradually changes to blue, and the subsequent addition of water liberates dimethylthianthren.

3 : 7-Dimethylthianthren dioxide,  $C_6H_3Me \begin{smallmatrix} SO \\ \diagup \diagdown \\ SO \end{smallmatrix} C_6H_3Me$ , obtained by the prolonged action of nitric acid on the thianthren, also crystallises from methyl alcohol in needles, and has m. p.  $194^\circ$ . The corresponding disulphone (Cohen and Skirrow, Trans., 1899, 75, 890) crystallises in cubes, m. p.  $286^\circ$ , and dissolves in concentrated sulphuric acid to a colourless solution.

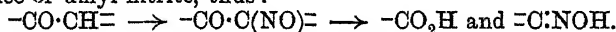
2 : 4 : 6 : 8-Tetrachloro-3 : 7-dihydroxythianthren,



crystallises from glacial acetic acid in colourless needles, m. p. above  $300^\circ$ .

Naphthathianthren [Dinaphthylene disulphide],  $C_{10}H_6 \begin{smallmatrix} S \\ \diagup \diagdown \\ S \end{smallmatrix} C_{10}H_6$ , crystallises from light petroleum in long, colourless needles, m. p.  $184^\circ$ .  
J. J. S.

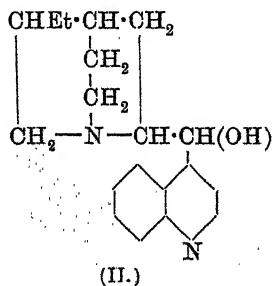
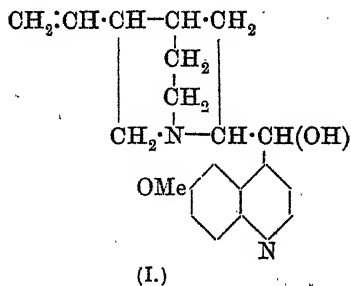
**Cinchona Alkaloids. X. Fission of the Ketones from Cinchona Bases.** PAUL RABE [with ERICH KULIGA and WILHELM NAUMANN] (*Annalen*, 1909, 365, 353—365. Compare this vol., i, 252).—Quinone is decomposed by nitrous acid (amyl nitrite), yielding quinic acid and an oxime,  $C_9H_{14}ON_2$ ; from this it follows that quinone contains the grouping  $-CO \cdot CH=$ , which breaks under the influence of amyl nitrite, thus :



The oxime when hydrolysed yields hydroxylamine and meroquinine, and is consequently  $\alpha$ -oximino- $\beta'$ -vinylquinuclidine. Quinine must therefore have the constitution represented by (I), likewise also quinidine, since it yields quinone when oxidised.

Cinchonidine gives rise to the same ketone as cinchonine, and must therefore have the same formula (compare Abstr., 1908, i, 100).

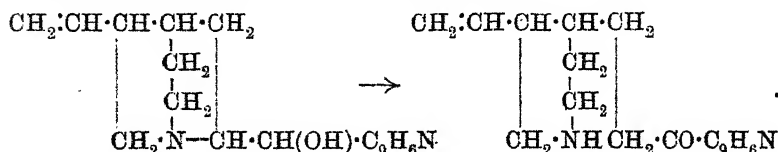
Hydrocinchoninone, when treated with nitrous acid, yields cinchonic acid and  $\alpha$ -oximino- $\beta'$ -ethylquinuclidine, consequently hydrocinchonine has the formula (II).



$\alpha$ -Oximino- $\beta'$ -ethylquinuclidine,  $C_9H_{16}ON_2$ , obtained by the action of amyl nitrite and sodium ethoxide on hydrocinchoninone, crystallises in

small, white needles, m. p. 133—134°. When boiled with hydrochloric acid, it yields cincholeuonic acid hydrochloride. W. H. G.

**Cinchona Alkaloids. XI. Identity of Methylcinchonine and Methylcinchonidine.** PAUL RABE (*Annalen*, 1909, 365, 366—376).—It follows from the author's work on the fission of the cinchona toxines (Abstr., 1907, i, 78, 790), and on the constitution of the cinchona alkaloids (preceding abstract), that the transformation of cinchonine into cinchotoxine takes place thus:



In other words, the cinchona alkaloids are 1:2-hydramines, and are characterised by a great tendency to pass into imino-ketenes. This property is of great importance in explaining the isomerism of cinchonine and cinchonidine. The hydrogen sulphates of these alkaloids yield the same substance, namely, cinchotoxine, when heated (compare von Miller and Rohde, Abstr., 1895, i, 434; 1901, i, 95). On the other hand, the recorded m. p.'s of methyl-, ethyl-, and benzyl-cinchonine are different from those of the corresponding alkylcinchonidines. In order to ascertain definitely whether the corresponding alkyl derivatives were different, the properties of several derivatives of methylcinchonine and methylcinchonidine were compared, and found to be identical. In future, therefore, these two bases are to be regarded as methylcinchotoxine.

[With FRITZ BRAASCH.]—*Methylcinchotoxine*, prepared either from cinchonine methiodide or cinchonidine methiodide, forms cubical crystals, m. p. 74—75°,  $[\alpha]_D^{20} + 35.28^\circ$  to  $+ 37.97^\circ$  (in chloroform). The methiodide has m. p. 197°: Claus and Müller give m. p. 201° (Abstr., 1881, 289). The *semicarbazone*,  $\text{C}_{21}\text{H}_{27}\text{ON}_5$ , forms white flakes, sinters at 204°, m. p. 210° (decomp.); the *picrate*,  $\text{C}_{26}\text{H}_{27}\text{O}_8\text{N}_5$ , forms yellow crystals, sinters at 95°, m. p. 120°; the *picrolonate*,  $\text{C}_{30}\text{H}_{32}\text{O}_6\text{N}_6$ , crystallises in nodules of small needles, m. p. 152—153°.

W. H. G.

**Methiodides of Cinchonic Esters and their Colour.** HERMAN DECKER and PERCY REMFREY (*J. pr. Chem.*, 1909, [ii], 79, 339—351).—*Ethyl cinchonate methiodide*,  $\text{C}_9\text{NH}_6\cdot\text{CO}_2\text{Et}\cdot\text{MeI}$ , is obtained by heating the ester and methyl sulphate for half an hour at 100°, dissolving the product in water, neutralising by sodium hydrogen carbonate, and adding solid potassium iodide. It separates from water in yellow crystals, m. p. 57°, containing  $2\text{H}_2\text{O}$ , which is readily lost, yielding red, anhydrous crystals, m. p. 63°. The red form gives a yellow solution in water, a red solution in alcohol, and a fine red solution in chloroform, thus showing the diminution of colour intensity with hydrate formation (compare Decker and Hock, Abstr., 1904, i, 450). The *picrate* forms yellow crystals, m. p. 140°. *Methyl cinchonate methiodide*,  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{NI}$ , m. p. 178°, obtained from the sodium salt

and methyl sulphate at 100° and precipitation by potassium iodide, forms red crystals. The red chloroform solution becomes pale yellow by the addition of a little water, and turns red again by the addition of solid potassium iodide. The *picrate*, m. p. 146°, and the *dichromate* are mentioned.

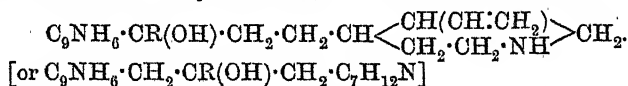
These ester-methiodides, unlike 1-methylquinolinium salts, which by treatment with alkali yield methylquinoline and methyltetrahydroquinoline (Decker, Abstr., 1903, i, 718), are hydrolysed with extraordinary ease by dilute ammonium or sodium hydroxide, yielding, after acidification and addition of potassium iodide, cinchonic acid methiodide, m. p. 224°. The esters, by warming with concentrated ammonium hydroxide, acidification, and addition of potassium iodide, yield *cinchonamide methiodide*,  $C_9NH_6 \cdot CO \cdot NH_2 \cdot MeI$ , m. p. 233°; the *picrate* has m. p. 198°.

The betaine of 1-methylcinchonic acid has m. p. 218° (Claus, 235°).

The paper also contains a reply to Hantzsch (this vol., ii, 198).

C. S.

**Constitution of Cinchonine (Cinchotoxine). I. Action of Organo-magnesium Haloids on Cinchonine:** *R*-Cinchotoxols. EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1909, [iii], 15, 32—43).—The groups present in the molecule of cinchonine capable of reacting with organo-magnesium haloids are:  $:N$ ,  $:NH$ ,  $:CO$ , and  $\cdot CH \cdot CH_2$ . The formula of  $\alpha$ -cinchonine being probably  $C_9NH_6 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CH}(\text{CH} \cdot \text{CH}_2) \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \end{smallmatrix} \text{CH}_2$ , the final product, after treating the complex organo-magnesium derivative with water, dilute acid, and finally ammonia, will have the constitution:



To the secondary alcohol, corresponding with cinchonine and not yet prepared, the author gives the name of cinchotoxol, its derivatives, represented by the above formula, being termed *R*-cinchotoxols.

[With NICOLA MELONE.]—The following complex compounds have been obtained: (1)  $C_{19}H_{21}ON_2 \cdot MgI, 3MgEtI$ , pale yellow powder, from cinchonine and magnesium ethyl iodide; (2)

$C_{19}H_{21}ON_2 \cdot MgBr, 3MgPhBr$ ;  
(3)  $C_{19}H_{21}ON_2 \cdot MgBr, 3Mg(C_{10}H_7)Br$ , from magnesium  $\alpha$ -naphthyl bromide.

*Ethylcinchotoxol*,  $C_{19}H_{22}N_2Et \cdot OH$ , is obtained as an amorphous, yellow powder, m. p. 84° (decomp.), having a bitter taste (compare Abstr., 1907, i, 1068).

*Phenylcinchotoxol*,  $C_{19}H_{22}N_2Ph \cdot OH$ , is a very bitter, amorphous substance, m. p. 104—106° (decomp.).

$\alpha$ -*Naphthylcinchotoxol*,  $C_{19}H_{22}N_2(C_{10}H_7) \cdot OH$ , is a yellowish-red, bitter, amorphous powder, m. p. 132—134°.

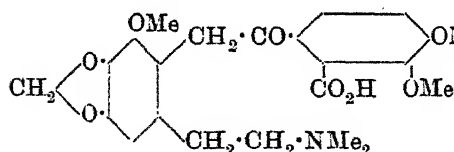
T. H. P.

**Decomposition of Laudanosine.** HERMAN DECKER and LUCAS GALATTY (*Ber.*, 1909, 42, 1179—1183).—An 85% yield of *laudanosomethine*,  $NMe_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_2(OMe)_2 \cdot CH \cdot CH \cdot C_6H_3(OMe)_2$ , is formed

when the quaternary salt obtained by the addition of methyl sulphate to laudanosine (Pictet and Athanescu, Abstr., 1900, i, 685) is boiled twice with ten times its weight of 15% potassium hydroxide solution for two hours, and the mixture extracted with ether after each boiling. It crystallises from light petroleum in long, felted needles, m. p. 96—97°. A small amount of a compound, m. p. about 320°, is formed at the same time, and yields soluble alkali salts. The methine is readily soluble in dilute acetic or sulphuric acids. The *hydrochloride*,  $C_{22}H_{30}O_4NCl \cdot H_2O$ , crystallises from hot water in long, felted needles, m. p. 220°. It is very sparingly soluble in cold water, and in the anhydrous form is very hygroscopic. The *platinichloride* decomposes readily, and melts at about 180°. The *hydrobromide* turns brown at 203°, and has m. p. 214°. When heated, the hydrochloride and hydrobromide yield dimethylamine. The *mercuribromide*,  $C_{22}H_{30}O_4NBr_3Hg$ , crystallises in lemon-yellow-coloured needles, m. p. 169—170°. The *picrate*,  $C_{22}H_{32}O_{11}N_4$ , is obtained as a precipitate on adding a benzene solution of picric acid to an ethereal solution of the base, and crystallises from boiling alcohol in dark red cubes, m. p. 181°.

When the methine is warmed with methyl sulphate and then with potassium hydroxide solution, trimethylamine is evolved and ether extracts from the liquid, *laudanosen* (*tetramethoxy-o-vinylstilbene*),  $CH_2:CH \cdot C_6H_2(OMe)_2 \cdot CH:CH \cdot C_6H_3(OMe)_2$ , which crystallises from warm alcohol in large needles, m. p. 94—95°. J. J. S.

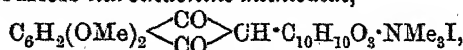
**Narceine.** MARTIN FREUND and PAUL OPPENHEIM (*Ber.*, 1909, 42, 1084—1101).—Of the two formulæ of narceine proposed by Freund



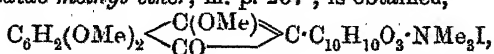
and Frankforter (Abstr. 1894, i, 58), the annexed one is to be accepted, the ambiguous position of the methoxyl group having been determined by Freund and Becker's de-

gradation of cotarnine to norcotarnone (Abstr., 1903, i, 572).

The presence of the group  $\cdot CH_2 \cdot CO \cdot$  is proved by the fact that the two methods by which deoxybenzoiccarboxylic acid is changed into 2-phenyldiketohydrindene are equally applicable for the conversion of narceine (which is a substituted deoxybenzoiccarboxylic acid according to the preceding formula) to narcindonine (Abstr., 1907, i, 235). The parallelism between 2-phenyldiketohydrindene and narcindonine is extended in the present communication. Since narcindonine and its sodium salt,  $C_{23}H_{24}O_7 \cdot NNa$ , are intensely red, they receive an enolic formula, whilst the salts of narcindonine with acids (*hydrochloride*, m. p. 255°; *hydriodide*, m. p. 246°) being colourless, have the ketonic formula. Colourless *narcindonine methiodide*,

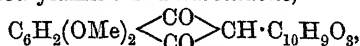


m. p. 217°, forms a red sodium salt, from which yellowish-red *narcindonine methiodide methyl ether*, m. p. 207°, is obtained,

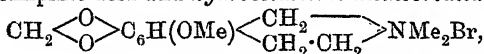


in which the presence of four methoxy-groups is shown by Zeisel's method.

Narcindonine methiodide is decomposed by boiling alcoholic sodium ethoxide into trimethylamine and *narcindone*,



m. p. 136—137°, which, like 2-phenyldiketohydrindene, is colourless, but forms coloured alkali salts. By the action of bromine on the sodium derivative of narcindonine in glacial acetic acid, *bromonarcindonine hydrobromide*,  $\text{C}_{23}\text{H}_{25}\text{O}_7\text{NBr}_2$ , is obtained, which separates from glacial acetic acid in colourless plates containing  $1\frac{1}{2}$  mols.  $\text{C}_2\text{H}_4\text{O}_2$ , darkening at 140° and decomposing at 150°. The corresponding base cannot be prepared. When the hydrobromide is evaporated with dilute sodium hydroxide, hemipinic acid and *hydrocotarnine methobromide*,

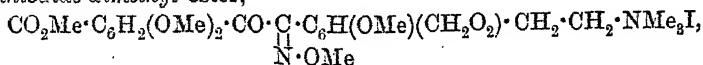


which decomposes at 221°, are produced. The identity of the latter is proved by converting it into the corresponding *methiodide*, m. p. 206°, which is identical with that obtained from hydrocotarnine. When the decomposition of bromonarcindonine hydrobromide is attempted by evaporating it with ammonium hydroxide, hemipinimide is formed together with the hydrobromide of a base, which is not decomposed by ammonium hydroxide, but is changed by concentrated sodium hydroxide into a base which immediately isomerises to hydrocotarnine methobromide.

When hydrocotarnine methobromide is heated with concentrated sodium hydroxide, it yields an oily base, which forms a *methiodide*,  $\text{C}_{14}\text{H}_{20}\text{O}_3\text{NI}$ , m. p. 193°. The base is proved to be Freund and Bamberg's *N*-methyldehydrocotarnine (Abstr., 1902, i, 556) by converting hydrocotarnine methiodide, obtained from cotarnine, into the methochloride, which, by decomposition with concentrated alkali, yields the same oily base, forming a methiodide, m. p. 193°, as is obtained above. The preceding transformations are all in harmony with the proposed formula of narceine, and afford evidence for the presence of the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$ . The latter point is also proved by the fact that narceine, like deoxybenzoin, forms an oximino-compound. Narceine, when treated with alcoholic sodium ethoxide and ethyl nitrite at 0° for two days in a closed vessel, yields *oximinonarceine*,  $\text{C}_{23}\text{H}_{26}\text{O}_9\text{N}_2$ , which has been obtained in three forms. The product obtained in the preceding preparation separates from alcohol in white plates, m. p. 178°, containing 1 mol.  $\text{C}_2\text{H}_6\text{O}$ . The yellow alkaline solution of this compound yields, by acidification with acetic acid, white plates, m. p. 173°, containing 1 mol.  $\text{H}_2\text{O}$ . The alcohol and the water in these two compounds are retained very firmly, but in boiling water both, without dissolving, yield free oximinonarceine, m. p. 196°. By prolonged heating at 115—120°, the forms containing water or alcohol yield a brown, viscous mass, from which have been isolated hemipinic acid and 2-cyano-3-methoxy-4:5-methylenedioxy-1-dimethyl-aminoethylbenzene,  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2$ , m. p. 50° (*hydrochloride*,  $\text{C}_{13}\text{H}_{16}\text{O}_3\text{N}_2\text{HCl}$ , m. p. 204°), which forms a *methiodide*,  $\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}_2\text{I}$ , decomposing at

225—226°, which is decomposed by dilute alkalis, yielding trimethylamine and Roser's 2-cyano-3-methoxy-4:5-methylenedioxy-1-vinylbenzene (Abstr., 1890, 528), obtained by the degradation of cotarnine.

Oximinonarceine, when digested on the water-bath with alcoholic sodium ethoxide and excess of methyl iodide, yields *oximinonarceine methiodide dimethyl ester*,

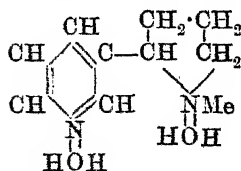


m. p. 247°, which is decomposed by boiling sodium hydroxide or ethoxide, yielding trimethylamine, hemipinic acid, and cyanomethoxy-methylenedioxyvinylbenzene. Oximinonarceine, when rapidly heated to 150°, decomposes into hemipinic acid, dimethylamine, and Roser's compound.

The most important results in the paper are the proof of the presence of the group  $\cdot\text{CH}_2\text{CO}$  in narceine, and the discovery that the degradation products of narceine are substances which have long been known as the products of the decomposition of narcotine.

C. S.

**The Binary System. Nicotine and Water.** DEMETRIUS TSAKALOTOS (*Bull. Soc. chim.*, 1909, [iv], 5, 397—404).—Hudson has shown (Abstr., 1904, ii, 446) that the complete mutual solubility curve of nicotine and water is a closed one, and this result has been confirmed by the author, although the temperatures of saturation were from 1° to 5° lower than those obtained by Hudson. The author has also measured the viscosity coefficients of mixtures of water and nicotine, and the resulting curve shows a maximum at the concentration of 78% of nicotine, and indicates the formation of a molecular combination between the water and nicotine (Abstr., 1908, ii, 260; i, 498, 598), probably of the annexed constitution.



The curve obtained by plotting the index of refraction against the concentration of the several mixtures is a straight line, as is also the curve similarly obtained for mixtures of aniline and *m*-cresol (Abstr., 1908, ii, 260); it follows, therefore, that the refraction is not affected by association in the liquid state.

M. A. W.

**2:5-Dimethylpyrroline-5-carboxylic Acid.** N. SCHLESINGER (*Ber.*, 1909, 42, 1159—1160. Compare Zelinsky and Schlesinger, Abstr., 1907, i, 720).—When the acid is mixed with twice its weight of lime and the mixture distilled in small quantities, 2:5-dimethylpyrroline and 2:5-dimethylpyrroline can be detected in the distillate.

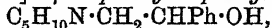
J. J. S.

**Formation of Double Salts in Non-aqueous Solvents.** LIVIO CAMBI (*Gazzetta*, 1909, 39, i, 361—370).—In addition to the salts already described (Abstr., 1907, i, 460), the author gives an account of the formation and properties of the following:  $\text{CuCl}_2 \cdot \text{LiCl} \cdot \text{C}_5\text{H}_5\text{N}$ , separating from pyridine;  $\text{NiI}_2 \cdot 2\text{NaI} \cdot 9\text{COMe}_2$ ;  $\text{CoI}_2 \cdot \text{CdI}_2 \cdot 6\text{C}_2\text{H}_5\text{O}$ ;  $\text{CoI}_2 \cdot 2\text{NaI} \cdot 6\text{Ac}_2\text{O}$ .

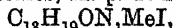
T. H. P.

**1:2-Hydramines.** I.  $\beta$ -Piperidyl- $\alpha$ -phenylethyl Alcohol. PAUL RABE and WILHELM SCHNEIDER (*Annalen*, 1909, 365, 377—382).—The stability of  $\beta$ -piperidyl- $\alpha$ -phenylethyl alcohol has been studied with the object of determining whether 1:2-hydramines in general behave like the alkaloids (compare this vol., i, 408); in other words, to see if compounds with the grouping  $\text{—N} \cdot \underset{\text{CH}_2}{\underset{|}{\text{C}}} \cdot \text{CH} \cdot \text{OH}$  disintegrate readily, owing to the separation of the nitrogen from the carbon atom. It is found that the sulphate of  $\beta$ -piperidyl- $\alpha$ -phenylethyl alcohol, when heated, does not decompose, neither does the hydramine undergo fission when boiled with acetic acid, nor when its methiodide is heated with sodium acetate in acetic acid; that is, this hydramine is far more stable than the alkaloids. Only in one respect does it resemble the alkaloids, and that is in the behaviour of the methiodide towards alkalis, whereby it is converted into acetophenone and 1-methylpiperidine.

[With FRITZ BRAASCH.]— $\beta$ -Piperidyl- $\alpha$ -phenylethyl alcohol,



prepared by reducing piperidylacetophenone with sodium and alcohol, has m. p. 67—68°, b. p. 188°/20 mm.; the following derivatives were prepared: *sulphate*, white needles, m. p. 140°; *picrate*, yellow, prismatic needles, m. p. 135°; *picrolonate*, orange needles, m. p. 163°; *platinichloride*, brownish-yellow scales, m. p. 194—195°; *methiodide*,



colourless needles, m. 136—137°.

W. H. G.

**Condensation of 4-Picoline, 2:6-Lutidine, and 2:4:6-Trimethylpyridine with Cinnamaldehyde and Anisaldehyde.** HEINRICH PROSKE (*Ber.*, 1909, 42, 1450—1457).—A small yield of  $\alpha$ -phenyl- $\delta$ -4-pyridylbutadiene,  $\text{C}_5\text{NH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CHPh}$ , is obtained by heating 4-picoline with cinnamaldehyde and a little freshly-melted zinc chloride for eight hours at 170—180°. The unaltered aldehyde and base can be removed by steam distillation, the latter after the solution has been made alkaline, and the condensation product finally extracted with ether. It crystallises from alcohol in colourless plates, m. p. 137—138°. The *aurichloride*,  $\text{C}_{15}\text{H}_{13}\text{N} \cdot \text{HAuCl}_4$ , forms a reddish-brown precipitate, m. p. 168—169°. The *mercurichloride* forms a lemon-yellow precipitate, which decomposes when recrystallised.

$\alpha$ -Phenyl- $\delta$ -(6-methyl-4-pyridyl)butadiene,  $\text{C}_{16}\text{H}_{15}\text{N}$ , obtained by heating 2:6-lutidine and cinnamaldehyde at 160—170° for eight hours, crystallises from alcohol, and has m. p. 103—104°. The *picrate* has m. p. 214—215°; the *platinichloride* crystallises from dilute alcohol in lemon-yellow needles, m. p. 173—174°, and the *aurichloride* forms a brownish-red, flocculent precipitate, m. p. 170—171°.

2:4:6-Trimethylpyridine, cinnamaldehyde, and zinc chloride yield  $\alpha$ -phenyl- $\delta$ -(4:6-dimethyl-2-pyridyl)butadiene,  $\text{C}_{17}\text{H}_{17}\text{N}$ , which is a pale red oil, b. p. 238—245°/21 mm. The *aurichloride* has m. p. 135—136°.

4-Methoxy-4-stilbazole,  $\text{C}_{14}\text{H}_{13}\text{ON}$ , is formed when 4-methylpyridine hydrochloride, anisaldehyde, and zinc chloride are heated for three days at 160—170°. It crystallises from dilute alcohol in glistening needles, m. p. 99—100°, after sintering at 91°.

The *mercurichloride*,  $C_{14}H_{13}ON, HCl, HgCl_2$ , forms a pale yellow, flocculent precipitate, m. p. 186—187°. The *hydrochloride* crystallises from water in small, yellow needles, m. p. 178—179°; the *nitrate* has m. p. 148—149°; the *platinichloride*, m. p. 201—203°, and the *aurichloride* forms an orange-coloured precipitate, which is decomposed on recrystallisation.

4'-Methoxy-6-methyl-2-stilbazole,  $C_{15}H_{15}ON$ , crystallises from benzene or amyl alcohol in brilliant, glistening plates, m. p. 181—182°. The *hydrochloride* forms lemon-yellow needles, m. p. 214—215° (decomp.); the *nitrate* forms pale yellow needles, m. p. 130—131°; the *picrate* has m. p. 175—176°; the *hydriodide* crystallises from alcohol in long, yellow, glistening needles, m. p. 216—217°; the *sulphate* forms orange-yellow needles, m. p. 209—210°; the *mercurichloride* melts at 209—210°, after sintering at 197°; the *aurichloride* separates from its alcoholic solution as yellowish-red needles, m. p. 170—171°, after sintering at 165°, and the *platinichloride* has m. p. 234°. When reduced with phosphorus and hydriodic acid, the base forms the *dihydro-derivative*,  $C_{15}H_{17}ON$ , which crystallises from alcohol and melts at 90—91°. The corresponding *hydrochloride* sinters at 270° and melts at 278—279°.

4'-Methoxy-6-methyl-2-stilbazole condenses with anisaldehyde in the presence of zinc chloride at 160—170°, yielding 2:6-di-p-methoxystyrylpyridine,  $C_{23}H_{21}O_2N$ . The *hydrochloride*,  $C_{23}H_{21}O_2N, HCl$ , crystallises from alcohol in golden-yellow plates, m. p. 148—149°. The *platinichloride* has m. p. 242—243°; the *mercurichloride*, m. p. 236—237°, and the *nitrate*, m. p. 148—149°.

p-Methoxy-4:6-dimethyl-2-stilbazole,  $C_{16}H_{17}ON$ , is a yellow oil, b. p. 230—235°/20 mm. The *mercurichloride* has m. p. 190°; the *platinichloride*, m. p. 176—177°, and the *aurichloride*, m. p. 175—176°.

2:6-Di-p-methoxystyryl-4-methylpyridine,  $C_{24}H_{23}O_2N$ , obtained from 2:4:6-trimethylpyridine and anisaldehyde, has m. p. 132—133°. The *mercurichloride* has m. p. 192°, after sintering at 177°; the *platinichloride*, m. p. 178—179°, and the *aurichloride*, m. p. 150—151°. Most of the salts cannot be recrystallised. J. J. S.

Condensation of  $\gamma$ -Picoline, 2:6-Lutidine, and  $\gamma$ -Collidine [2:4:6-Trimethylpyridine] with Piperonaldehyde and Salicylaldehyde. WALTHER BRANSCH (*Ber.*, 1909, 42, 1193—1197).— $\gamma$ -Picoline (4-methylpyridine) and piperonaldehyde condense when heated with zinc chloride under pressure at 180°, yielding  $\gamma$ -piperonylidenepicoline,  $C_{14}H_{11}O_2N$ , obtained as a white, flocculent substance, m. p. 98°. The following salts were prepared: *hydrochloride*,

$C_{14}H_{11}O_2N, HCl$ ,  
long, yellow needles, m. p. 238°; *mercurichloride*,

$C_{14}H_{11}O_2N, HCl, HgCl_2$ ,  
pale yellow needles, m. p. 187°; *platinichloride*,

$(C_{14}H_{11}O_2N)_2, H_2PtCl_6$ ,  
dark yellow needles, m. p. 204°; *aurichloride*,  $C_{14}H_{11}O_2N, HAuCl_4$ ,  
reddish-brown powder, m. p. 170°.

*Piperonylidene-2:6-lutidine*,  $C_{15}H_{13}O_2N$ , prepared from piperonaldehyde and 2:6-lutidine (2:6-dimethylpyridine), is a white substance, m. p. 109°; the crystalline *hydrochloride* has m. p. 275°; the

*mercurichloride* forms small, dark yellow needles, m. p. 225°; the *platinichloride* has m. p. 215°; the *aurichloride* crystallises in reddish-brown needles, m. p. 185°.

*Piperonylidene-2:4:6-trimethylpyridine*,  $C_{16}H_{15}O_2N$ , prepared from 2:4:6-trimethylpyridine and piperonaldehyde, is a pale yellow, viscid oil, b. p. 55—60°/50—60 mm.; the *hydrochloride* crystallises in slender, white, silky needles, m. p. 262°; the *mercurichloride* forms pale yellow needles, m. p. 223—224°; the crystalline *platinichloride* has m. p. 224°; the *aurichloride* is a brownish-red, flocculent substance, m. p. 156°. When 2:4:6-trimethylpyridine is heated with a large excess of piperonaldehyde it yields *dipiperonylidene-2:4:6-trimethylpyridine*  $C_{24}H_{19}O_4N$ , crystallising in white needles, m. p. 154°; the *mercurichloride*,  $C_{24}H_{19}O_4N \cdot HCl \cdot HgCl_2$ , forms reddish-brown needles, m. p. 236—237°.

*2'-Hydroxy-4-stilbazole*,  $C_{13}H_{11}ON$ , prepared from salicylaldehyde and  $\gamma$ -picoline, forms white flakes, m. p. 120—122°, b. p. 200—210°/50—60 mm.

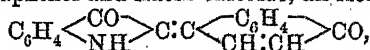
*2'-Hydroxy-6-methyl-2-stilbazole*,  $C_{14}H_{13}ON$ , prepared from salicylaldehyde and 2:6-lutidine, crystallises in long, white needles, m. p. 199°; the *hydrochloride*,  $C_{14}H_{13}ON \cdot HCl$ , forms long, pale yellow needles, which do not melt at 300°; the *mercurichloride* is a pale yellow, flocculent substance, m. p. 155°; the *platinichloride* is a yellow powder, which does not melt at 300°; the *aurichloride* is a brown powder, m. p. 177—178°.

*2'-Hydroxy-4:6-dimethyl-2-stilbazole*,  $C_{15}H_{15}ON$ , obtained by the condensation of 2:4:6-trimethylpyridine with salicylaldehyde, is a pale yellow oil, b. p. 170—175°/20—25 mm.; the *hydrochloride* forms long, yellow needles, m. p. 260°; the *mercurichloride* is a yellow, flocculent substance, m. p. 160°; the *platinichloride* has m. p. 204—205°.

The bases described in this paper are decomposed when reduced with sodium and ethyl or amyl alcohol. W. H. G.

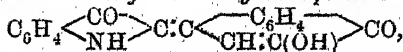
**Indigoid Dyes. IV. Indigoid and Indolignoid Dyes of the Naphthalene Series and their Decomposition Products (Hydroxynaphthaldehydes).** A. BEZDŽIK and PAUL FRIEDLÄNDER (*Monatsh.*, 1909, 30, 271—286. Compare Abstr., 1908, i, 673, 674).

—In addition to the indigoid dye,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CO} \cdot C_6H_4 \\ \text{CH}:\text{CH} \end{smallmatrix}$ , obtained from  $\alpha$ -naphthol and isatin chloride, an isomeride,



is also formed. These two compounds have very similar properties; the latter is characterised by the chain  $-\text{CO} \cdot \text{C}:\text{C} \cdot \text{C}:\text{C} \cdot \text{CO}-$ . A series of substances containing this chain have been prepared, and the group name *lignone* is proposed, the above compound being termed by the authors 2-indole-1-naphthaleneindolignone.

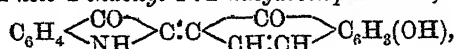
*3-Hydroxy-4-keto-1-indoxyl-1:4-dihydronaphthalene*,



prepared by the interaction of 1:2-dihydroxynaphthalene and isatin

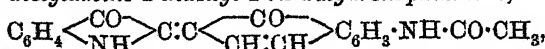
chloride, forms glistening, brown needles, and dyes mordanted fabrics a greenish-blue.

*5-Hydroxy-1-keto-2-indoxyl-1 : 2-dihydronaphthalene,*



is obtained in copper-red-coloured, glistening needles by the interaction of 1:5-dihydroxynaphthalene with  $\alpha$ -isatin anilide and acetic anhydride. When heated, it forms a carmine-red vapour; sodium hydroxide converts it into 1:5-dihydroxy-2-naphthaldehyde. It dissolves in concentrated sulphuric acid with a blue coloration, and is sulphonated on heating.

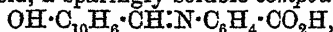
*1-Keto-5-acetylamino-2-indoxyl-1 : 2-dihydronaphthalene,*



prepared from 5-amino-1-naphthol and  $\alpha$ -isatinanilide, forms dark violet needles. The isomeric 1-keto-4-acetylamino-2-indoxyl-1 : 2-dihydro-

naphthalene,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C}:\text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}:\text{C}(\text{NHAc}) \end{array} \text{C}_6\text{H}_4$ , is obtained from 4-acetylamino-1-naphthol and isatinanilide.

*1-Hydroxy-2-naphthaldehyde*, prepared by heating 1-oxy-2-indoxyl-naphthalene with 10% sodium hydroxide, crystallises in greenish-yellow needles, m. p. 59°, has a characteristic cinnamon-like odour, dissolves in alkalis with a yellow colour, and gives a green coloration with ferric chloride. The *oxime* crystallises in faintly yellow-coloured needles, m. p. 145°; the *phenylhydrazone* forms plates, m. p. 115—116°. With anthranilic acid, a sparingly soluble compound,



is obtained, crystallising in bright red, quadratic plates (decomp. above 200°). *1-Methoxy-2-naphthaldehyde*, prepared by means of methyl sulphate, forms colourless crystals, m. p. 47°. *1:2-a-Naphtha-*

*pyrone*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{O} - \text{CO} \\ | \quad | \\ \text{CH}:\text{CH} \end{array}$ , prepared by boiling the hydroxyaldehyde with

sodium acetate and acetic anhydride, forms faintly coloured needles, m. p. 138°, is insoluble in sodium carbonate, slightly volatile in steam, and has a slight, though definite, coumarin odour.

*1:2-Dimethoxynaphthalene*, prepared by methylation with methyl sulphate, has b. p. 278—280°, m. p. 31°, and forms a picrate, crystallising in red needles, m. p. 97°. A mixture of  $\beta$ -methoxy- $\alpha$ -naphthol and  $\alpha$ -methoxy- $\beta$ -naphthol is obtained at the same time, the former of which is very easily oxidised in alkaline solution, and could not be isolated.  $\alpha$ -Methoxy- $\beta$ -naphthol forms colourless, stout, monoclinic plates, m. p. 90.5°.

*1-Hydroxy-4-methoxy-2-naphthaldehyde* has, like methylgentisic aldehyde, an intense citron-yellow colour, and dyes the skin a fast yellow. It gives a dark green coloration with ferric chloride, and dissolves in alkalis, giving orange-yellow solutions.

*3-Chloro-4-hydroxy-1-naphthaldehyde* is obtained from the indolignone of 2-chloro- $\alpha$ -naphthol; it forms colourless needles, m. p. 245° (decomp.).

*2:5-Dihydroxy-2-naphthaldehyde* forms minute, voluminous needles, m. p. 215°, and gives a dark olive-green ferric chloride coloration.

1-Hydroxy-5-methoxy-2-naphthaldehyde crystallises in citron-yellow needles, m. p. 128°. E. F. A.

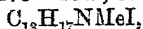
**Binuclear Quinones.** PAUL FRIEDLÄNDER (*Ber.*, 1909, 42, 1058—1062. Compare preceding abstract).—3-Hydroxy-4-keto-1-indoxyl-1:4-dihydronaphthalene,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{CH}:\text{C}(\text{OH}) \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO}$ , prepared from 1:2-dihydroxynaphthalene and isatin chloride, forms dark green needles of metallic lustre or lustrous, bronze needles; it dissolves in alkalis with a dark green or olive-yellow coloration, and dyes mordanted fabrics a greenish-blue.

10-Keto-9-indoxylantracene,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO}$ , prepared from isatin chloride and anthranol, forms dark brownish-red or transparent, ruby-red crystals.

10-Keto-9-thionaphthylantracene,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{S} \end{smallmatrix} \text{C}:\text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO}$ , forms lustrous, brown needles, m. p. 219°. The above dyes are somewhat redder than the corresponding indigoids, and, like them, are decomposed by alkalis into anthranilic acid and an hydroxyaldehyde, which in this case belongs to the para-series E. F. A.

**Action of Grignard Reagents on Quaternary Ammonium Halides.** MARTIN FREUND and LUDWIG RICHARD (*Ber.*, 1909, 42, 1101—1121).—Quaternary ammonium halides, which react with alkalis to form  $\psi$ -bases, interact easily with organo-magnesium halides, yielding substances which differ from the  $\psi$ -bases by containing a hydrocarbon residue in place of the hydroxyl group. Quinoline, cotarnine, hydrastinine, berberine, phenylacridine, and crystal-violet have been examined already (*Abstr.*, 1905, i, 151, 156, 159). The present paper is a continuation of the subject, and deals mainly with two questions, whether the entrant radicle is always attached to the 2-carbon atom in quinoline derivatives, and secondly, what is the action when the 2-carbon atom is already substituted. The interaction of quinoline methiodide and ethereal magnesium ethyl bromide leads to the formation of 1-methyl-2-ethylidihydroquinoline,  $C_6H_4 \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{NMe} \cdot \text{CHEt} \end{smallmatrix}$ , b. p. 265°, or 141—142°/21 mm. (*platinichloride*,  $2C_{12}H_{15}N \cdot H_2PtCl_6$ , m. p. 176°), which is reduced by tin and 20% hydrochloric acid to the corresponding tetrahydroquinoline,  $C_{12}H_{17}N$ , b. p. 265—267°, of which the *hydrochloride*, *hydrobromide*, and *hydriodide* have m. p. 207°, 196°, and 193° respectively. In a similar way, quinoline methiodide and magnesium methyl iodide yield 1:2-dimethyldihydroquinoline (*platinichloride*, m. p. 178°), which is reduced to 1:2-dimethyltetrahydroquinoline. Since it has been already shown (*loc. cit.*) that 2-phenyl-1-methyldihydroquinoline is produced in the same way, it may be stated that the action of organo-magnesium halides on quaternary quinolinium halides is a general method for the production of 2-substituted dihydroquinolines, which are reduced to the corresponding tetrahydroquinolines.

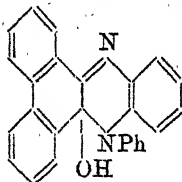
The presence of a substituent in the 2-position does not appear to influence the reaction, since 2-methylquinoline methiodide reacts in an analogous manner with magnesium methyl, ethyl, or phenyl halides. 1:2:2-Trimethyldihydroquinoline,  $C_{12}H_{15}N$ , b. p. 273—275°, forms a *picrate*, m. p. 138°, and is reduced to the *tetrahydro*-compound,  $C_{12}H_{17}N$ , b. p. 269—270° (*picrate*, m. p. 178°). 1:2-Dimethyl-2-ethylidihydroquinoline, b. p. 279—284°, forms a *methiodide*,



m. p. 260—261°, and is reduced to the *tetrahydro*-compound, b. p. 278—284°, of which the *hydrochloride* and the *picrate* have m. p. 208° and 138° respectively. 2-Phenyl-1:2-dimethyldihydroquinoline, b. p. 310—330° (decomp.), forms a *picrate*, m. p. 170—172°.

The preceding rule appears to be applicable to azonium bases, for Kehrman's 1:2:3-triphenylquinoxaline bromide, which forms a  $\psi$ -base (Hantzsch and Kalb, Abstr., 1900, i, 113), reacts with magnesium ethyl iodide (2 mols.) to yield 1:2:3-triphenyl-2-ethyl-dihydroquinoxaline,  $CPhEt \left\langle \begin{array}{c} CPh \cdot N \\ NPh \cdot C_6H_4 \end{array} \right.$ , m. p. 198—199°.

Phenazonium compounds have also been examined. Flavinduline bromide, which forms a  $\psi$ -base (Hantzsch and Osswald, Abstr., 1900, i, 256), reacts with organo-magnesium halides in a way that does not confirm Hantzsch and Osswald's formula of the  $\psi$ -base, but



points rather to the annexed constitution, for yellow basic compounds, having a hydrocarbon residue in the place of the hydroxyl group in the figure, are produced together with colourless, non-basic isomerides, in which the hydrocarbon residue has wandered to the unsubstituted nitrogen atom. For example, the interaction of flavinduline bromide and magnesium benzyl chloride leads to the formation of a mixture of *N*-phenyl- $\alpha$ -benzyl-dihydrophenanthraphenazine,  $C_{33}H_{24}N_2$ , m. p. 175—179°, which forms yellow crystals and a red hydrochloride, and *N*-phenyl-*N'*-benzyl-dihydrophenanthraphenazine,  $C_{33}H_{24}N_2$ , m. p. 185°, which is colourless and does not form salts. The former of these two compounds is changed to the latter at 120—130°. Flavinduline bromide reacts, (a) with magnesium ethyl bromide (5 mols.) to form *N*-phenyl- $\alpha$ -ethyl-dihydrophenanthraphenazine,  $C_{28}H_{22}N_2$ , m. p. 172°, which exists only in the yellow modification and forms a *hydrochloride*, m. p. 196°, and a *hydrobromide*, m. p. 190°; (b) with magnesium methyl iodide to form the corresponding yellow *methyl* compound,  $C_{27}H_{20}N_2$ , m. p. 176°, which also forms red salts, and (c) with magnesium phenyl bromide to form colourless crystals of *N*:*N'*-diphenyldihydrophenanthraphenazine,  $C_{32}H_{22}N_2$ , m. p. 243°, which does not form salts.

Brilliant-green (the hydrochloride of tetraethyldiaminotriphenyl-carbinol) behaves like crystal-violet (Freund and Beck, *loc. cit.*), yielding with magnesium benzyl chloride, tetraethyldiaminotriphenyl-benzylmethane,  $CH_3Ph \cdot CPh(C_6H_4 \cdot NEt_2)_3$ , m. p. 151°, which forms colourless crystals and pale green solutions; the *hydriodide* has m. p. 140°, and the *methiodide*, m. p. 148°. Brilliant-green reacts

in a similar way with magnesium ethyl bromide, forming tetraethyl-diaminotriphenylethylmethane, which is isolated as the *hydrogen sulphate*,  $C_{29}H_{38}N_2 \cdot 2H_2SO_4$ , m. p.  $205^\circ$  (the *hydriodide* has m. p.  $220-223^\circ$ ), and with magnesium propyl iodide, forming the corresponding propyl compound, which is also isolated as the *hydrogen sulphate*,  $C_{30}H_{40}N_2 \cdot 2H_2SO_4$ , m. p.  $230^\circ$ . C. S.

**Formation of Acid Chlorides.** HANS MEYER and RICHARD TURNAU (*Ber.*, 1909, 42, 1163—1169. Compare Abstr., 1906, i, 138).—Both malonic and isosuccinic acids give good yields of chlorides by the action of thionyl chloride. 2-Hydroxy-3-methylcinchonic acid yields the normal chloride when heated with thionyl chloride in open vessels; when heated under pressure, however, it yields the chloride of 2-chloro-3-methylcinchonic acid. The formation of this chloro-derivative is undoubtedly due to the action of the hydrogen chloride on the hydroxy-chloride.

The differences noticed by Meyer and Turnau (Abstr., 1905, i, 155, 666; 1907, i, 344), and Besthorn and Ibele (*ibid.*, 1905, i, 612; 1906, i, 605), in the action of thionyl chloride on quinoline-2-carboxylic acid are accounted for by the fact that the chloride used by Meyer and Turnau contained small amounts of sulphur dioxide, which readily transforms Besthorn and Ibele's unimolecular quinaldinic chloride (m. p.  $97-98^\circ$ ) into Meyer's polymeride, m. p.  $170^\circ$ .

When the thionyl chloride is distilled over dimethylaniline, the sulphur dioxide is removed, and the purified product yields no trace of the polymeride. The polymeric chloride is formed from quinoline-2-carboxylic acid, also, when the acid has not been recrystallised, owing to the fact that the impure acid contains traces of nitric acid.

J. J. S.

**Synthesis of Ethyl Quinaldineoxalate and Lepidineoxalate by means of Potassium Ethoxide.** WILHELM WISLICENUS and EMIL KLEISINGER (*Ber.*, 1909, 42, 1140—1143. Compare Abstr., 1897, i, 488).—Potassium ethoxide is a more efficient condensing agent than sodium ethoxide. When a cold alcoholic ethereal solution of potassium ethoxide is treated with equal molecular quantities of ethyl oxalate and quinaldine, the *potassium* derivative of ethyl quinaldineoxalate,  $C_9H_8 \cdot CH \cdot C(OK) \cdot CO_2Et$ , is obtained as a hygroscopic, yellow substance, which is decomposed by water, the liberated potassium hydroxide hydrolysing one-half of the resulting ethyl quinaldineoxalate into its constituents. The potassium derivative, by treatment with the calculated quantity of dilute sulphuric acid, yields a colourless *sulphate*, from which ammonium hydroxide liberates *ethyl quinaldineoxalate*,  $C_{14}H_{18}O_3N$ , m. p.  $130-132^\circ$ . The ester crystallises in yellow needles or prisms, and has pronounced amphoteric properties; it is hydrolysed by 6% sulphuric acid, yielding the acid (*loc. cit.*), which decomposes at  $167-168^\circ$ .

The corresponding 4-methylquinoline derivatives are obtained in a similar way. 4-Methylquinolineoxalic acid has m. p.  $224-225^\circ$  (decomp.); the *ethyl* ester has m. p.  $194-196^\circ$ . C. S.

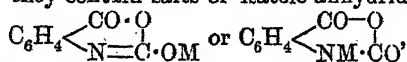
**Preparation and Reactivity of 3-Methylquinoline.** WILHELM WISLIGENUS and HEINRICH ELVERT (*Ber.*, 1909, 42, 1144—1145).—By mixing *o*-aminobenzaldehyde and propaldehyde, a yellowish-white, crystalline substance,  $\text{CHEt}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO})_2$ , m. p. 103—105°, is obtained. 3-Methylquinoline is obtained in 80—85% yield by heating molecular quantities of propaldehyde and *o*-aminobenzaldehyde at 220° for one hour; it does not condense with ethyl oxalate (preceding abstract). C. S.

**Occurrence of Hydroacridine in Coal Tars.** HERMAN DECKER and GEORGES DUNANT (*Ber.*, 1909, 42, 1178—1179).—Coal tars appear to contain dihydroacridine, since the crude acridine when treated with excess of methyl sulphate and then with sodium carbonate yields a precipitate of 10-methyldihydroacridine (Pictet and Patry, *Abstr.*, 1902, i, 644). J. J. S.

**Hofmann's Reaction. IV. Behaviour of Isatoic Anhydride with Alkalis and with Barium Hydroxide.** ERNST MOHR (*J. pr. Chem.*, 1909, [ii], 79, 281—329. Compare *Abstr.*, 1905, i, 890; 1906, i, 252, 357; this vol., i, 190).—The paper deals mainly with the remarkable changes which isatoic anhydride undergoes in alkaline solutions of different concentrations. The chief result is that the anhydride yields two series of salts.

Solutions of the salts of the one series are obtained by dissolving isatoic anhydride (1 mol.) in 5 or more molecules of dilute alkali, for example, sodium hydroxide, at the ordinary temperature. Such solutions yield carbon dioxide and anthranilic acid by acidification. That the solution before acidification cannot contain sodium carbonate and anthranilate is proved by the following experiment. Two solutions, one of isatoic anhydride and the other of anthranilic acid, dissolved in equal amounts of barium hydroxide, are treated with calcium hypochlorite; the former remains clear for a few minutes, and then slowly develops a rose-red colour, whilst the solution of barium anthranilate gives a deep bluish-violet coloration. The solution obtained from isatoic anhydride and an excess of alkali hydroxide probably contains the normal isatoate; it is proved experimentally that such a solution decomposes slowly in the presence of excess of alkali, rapidly with only a slight excess, yielding carbonate and anthranilate.

Salts of the second series are obtained by dissolving 1 mol. of isatoic anhydride in a small excess of an alkali hydroxide at the lowest convenient temperature. Such solutions have a blue fluorescence and regenerate the anhydride by immediate acidification, or by treatment with a saturated solution of ammonium chloride or of sodium hydrogen carbonate at 0°; they contain salts of isatoic anhydride,

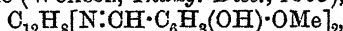


and not normal isatoates, as Erdmann supposes. The potassium and the barium salts have been isolated. The solutions of such salts are very unstable; at the ordinary temperature isatoic anhydride is spontaneously deposited, and the solution contains carbonate and anthranoylanthranilate, whilst, by boiling, carbon dioxide is evolved,

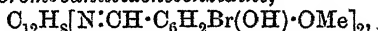
and the filtered solution yields pure anthranoylanthranilic acid by acidification. C. S.

**Vanillidene- and Piperonylidene-benzidines.** HENRY A. TORREY and E. D. CLARKE (*J. Amer. Chem. Soc.*, 1909, 31, 583—585).—When a solution of vanillin is treated with benzidine, a precipitate of vanillidenebenzidine is produced. This observation led to a study of the reaction in the hope that it might be of value for the estimation of vanillin. It was found, however, that the method was unsatisfactory, since both mono- and di-vanillidene derivatives of benzidine are produced according to the amount of benzidine added.

*Vanillidenebenzidine*,  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , m. p. about  $181^\circ$ , forms bright yellow crystals and dissolves in glacial acetic acid, giving a red solution, from which it separates on cooling as a moss-like mass of crimson crystals; when the latter are washed with dilute alcohol, the substance regains its original yellow colour. Di-vanillidenebenzidine (Wolfson, *Inaug. Diss.*, 1905),

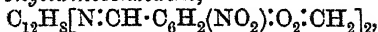


m. p.  $220-221.5^\circ$ , is a yellow substance. On treating this compound with a hot alcoholic solution of salicylaldehyde, the vanillidene complex is replaced by the salicylidene group. By the action of benzidine on bromovanillin, *bisbromovanillidenebenzidine*,



is obtained as a yellow, crystalline substance, which is turned red by acids and decomposes slowly at  $232^\circ$ .

*Bis-6-nitropiperonylidenebenzidine*,



obtained by mixing hot alcoholic solutions of 6-nitropiperonal and benzidine, is a dark yellow, crystalline substance, which decomposes at  $273^\circ$ . *Bisbromopiperonylidenebenzidine*,  $\text{C}_{12}\text{H}_8[\text{N} : \text{CH} \cdot \text{C}_6\text{H}_2\text{Br} : \text{O}_2 : \text{CH}_2]_2$ , m. p.  $257^\circ$  (decomp.), forms yellow crystals. E. G.

**Hydrazones of Sugars.** A. RECLAIRE (*Ber.*, 1909, 42, 1424. Compare Abstr., 1908, i, 1013).—*Xylose-o-nitrophenylhydrazone*,  $\text{C}_{11}\text{H}_{15}\text{O}_6\text{N}_3$ , crystallises from methyl alcohol in long, red needles, m. p.  $123^\circ$ . *Sorbose-o-nitrophenyllosazone*,  $\text{C}_{15}\text{H}_{22}\text{O}_8\text{N}_6$ , is a dark red powder, m. p.  $211-212^\circ$ . J. V. E.

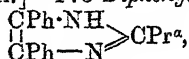
**Method of Formation of Benzoylphenylhydrazine.** ANGELO ANGELI and VINCENZO CASTELLANA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 322—324).—The great similarity in behaviour between hydroxylamine derivatives and hydrazine derivatives renders it almost certain that the action of alkalis on phenylsulphonehydrazobenzene, studied by Hantzsch and Glogauer (Abstr., 1898, i, 78), which proceeds according to the equation  $\text{R} \cdot \text{SO}_2 \cdot \text{NPh} \cdot \text{NHPh} = \text{R} \cdot \text{SO}_2\text{H} + \text{NPh} \cdot \text{NPh}$ , is analogous to the action of an alkali on the sulphydroxamic acids, an intermediate compound,  $\text{NHPh} \cdot \text{NPh} \cdot \text{OH}$ , being formed, which loses water, yielding azobenzene.

The authors have studied the action of potassium hydroxide on benzenesulphonephenylhydrazine,  $\text{SO}_2\text{Ph} \cdot \text{NH} \cdot \text{NHPh}$ , which yields an unstable salt, rapidly decomposing according to the equation  $\text{NHPh} \cdot \text{NH} \cdot \text{OH} = \text{C}_6\text{H}_6 + \text{N}_2 + \text{H}_2\text{O}$ . It is found, indeed, that with

benzaldehyde, this unstable intermediate compound yields benzoyl-phenylhydrazine,  $\text{NHPh} \cdot \text{NH} \cdot \text{OH} + \text{Ph} \cdot \text{CHO} = \text{NHPh} \cdot \text{NHBz} + \text{H}_2\text{O}$ .  
T. H. P.

**Glyoxalines.** BR. RADZISZEWSKI (*Bull. Acad. Sci. Cracow*, 1909, 213—219).—Glyoxalines may be prepared by saturating an alcoholic solution of benzil and an aldehyde with ammonia gas and precipitating with water. The methyl derivatives are prepared by warming the alcoholic solution with an excess of methyl iodide.

[With BR. WYSOZKAŃSKI.]—4:5-Diphenyl-2-propylglyoxaline,



prepared from benzil and butaldehyde, forms pale yellow needles, m. p. 205.5°. This and the following glyoxalines oxidise slowly in alkaline alcoholic solutions with phosphorescence. The *hydrochloride* forms colourless crystals, m. p. 233.5°; the *oxalate*, needles, m. p. 210°. The *methyl ether*,  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{Me}$ , melts below 110°.

[With M. BEISER.]—4:5-Diphenyl-2-isopropylglyoxaline,  $\text{C}_{18}\text{H}_{18}\text{N}_2$ , forms pale yellow needles, m. p. 246°. The *hydrochloride*, needles, m. p. 227°; the *platinichloride*,  $(\text{C}_{18}\text{H}_{18}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ , orange crystals, m. p. above 290° (decomp.), and the *methyl ether*, m. p. 97°.

[With H. BUKOWSKA.]—4:5-Diphenyl-2-amylglyoxaline,  $\text{C}_{20}\text{H}_{22}\text{N}_2$ , from hexaldehyde, forms colourless needles, m. p. 252°. The *hydrochloride*, m. p. 161°; *platinichloride*,  $(\text{C}_{20}\text{H}_{22}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ , yellow crystals, m. p. 272° (decomp.), and *methyl ether*, m. p. 127°.

[With A. JAKALO.]—4:5-Diphenyl-2-hexylglyoxaline,  $\text{C}_{21}\text{H}_{24}\text{N}_2$ , forms colourless needles, m. p. 167°; *hydrochloride*, scales, m. p. 133°; *picrate*, needles, m. p. 170°; *oxalate*,  $(\text{C}_{21}\text{H}_{24}\text{N}_2)_2 \cdot \text{C}_2\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , m. p. 190°; *methyl ether*, m. p. 164°.

[With S. STENZEL.]—4:5-Diphenyl-2-o-tolylglyoxaline,  $\text{C}_{23}\text{H}_{18}\text{N}_2$ , from o-tolualdehyde, m. p. 252°; *hydrochloride*, m. p. 120°; *platinichloride*, decomp., 225°; *methyl ether*, m. p. 259°.

4:5-Diphenyl-2-m-tolylglyoxaline, m. p. about 300°; *hydrochloride*, m. p. 125°; *platinichloride*, m. p. 230° (decomp.); *ethyl ether*,  $\text{C}_{25}\text{H}_{17}\text{N}_2\text{Et}$ , m. p. above 310°.

[With J. ROHM.]—The following compounds are better prepared by heating the aldehyde with benzil, ammonium carbonate, and a little alcohol at 180° for six to eight hours. 4:5-Diphenyl-2-p-tolylglyoxaline forms colourless crystals, m. p. 233°; *hydrochloride*, m. p. 120°; *platinichloride*, decomp. about 250°; *methyl ether*, m. p. 217°. 4:5-Diphenyl-2-hydroxymethoxyphenylglyoxaline,  $\text{C}_{25}\text{H}_{18}\text{O}_2\text{N}_2$ , from vanillin, m. p. 243°; *hydrochloride*, m. p. 154°; *platinichloride*, decomp. about 230°; *methyl ether*, m. p. 230°.

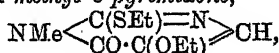
4:5-Diphenyl-2-α-naphthylglyoxaline,  $\text{C}_{25}\text{H}_{18}\text{N}_2$ , m. p. 283°; *hydrochloride*, decomp., 180°; *platinichloride*, decomp. about 230°; *methyl ether*, m. p. 291°.  
C. H. D.

**Electrolytic Reduction of a Nitro-derivative of Pyrazolone.** GOTTFRIED KÜMMEL and E. REMY (*Zeitsch. Elektrochem.*, 1909, 15, 254. Compare Abstr., 1907, i, 145).—Nitro-1-phenyl-3-pyrazolone dissolved in alcoholic sulphuric acid is electrolysed with a large

cathode and small anode of lead at 80°. The reduction takes places in exactly the same way as is the case with aromatic nitro-compounds, the final product being the amino-derivative, of which more than 86% of the theoretical yield is obtained. *Amino-1-phenyl-3-pyrazolone* forms colourless needles, m. p. 257°. T. E.

**Pyrimidines. XLII. Synthesis of 5-Hydroxy-1-methyluracil.** TREAT B. JOHNSON and D. BREESE JONES (*J. Amer. Chem. Soc.*, 1909, 31, 590—596).—Johnson and McCollum (Abstr., 1906, i, 704) have obtained 5-hydroxyuracil (*isobarbituric acid*) in quantitative yield by the hydrolysis of 5-ethoxy-2-ethylthiol-6-pyrimidone. Johnson and Jones (this vol., i, 60) have shown that *N*-alkyl derivatives of this thiolpyrimidine can be readily prepared, and that, on hydrolysis, they yield *N*-alkyl derivatives of 5-hydroxyuracil; 5-hydroxy-1-benzyluracil and 5-hydroxy-3-benzyluracil were prepared in this way. The present investigation was carried out with the object of obtaining the *N*-methyl derivatives of 5-ethoxy-2-ethylthiol-6-pyrimidone and submitting them to hydrolysis.

When 5-ethoxy-2-ethylthiol-6-pyrimidone is treated with methyl iodide, a mixture of the 1- and 3-methyl derivatives is produced containing about 70% of the theoretical yield of the 1-methyl compound. *5-Ethoxy-2-ethylthiol-1-methyl-6-pyrimidone*,



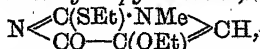
m. p. 50°, crystallises in plates; it combines with potassium iodide to form the compound,  $3\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2\text{S}_2\text{KI}$ . When this pyrimidine is hydrolysed with hydrobromic acid, it is converted into a mixture of

*2-thio-5-hydroxy-1-methyluracil*,  $\text{NMe} \begin{array}{c} \text{CS} - \text{NH} \\ \text{CO} \cdot \text{C(OH)} \end{array} \text{CH}$ , which forms slender prisms and has no definite m. p., and *2:6-diketo-5-ethoxy-1-methylpyrimidine*,  $\text{NMe} \begin{array}{c} \text{CO} - \text{NH} \\ \text{CO} \cdot \text{C(OEt)} \end{array} \text{CH}$ , m. p. about 240° (decomp.),

which crystallises in short prisms. If *2:6-diketo-5-ethoxy-1-methylpyrimidine* or *5-ethoxy-2-ethylthiol-1-methyl-6-pyrimidone* is heated with concentrated hydrochloric acid at 120—130°, *5-hydroxy-1-methyluracil*,  $\text{NMe} \begin{array}{c} \text{CO} - \text{NH} \\ \text{CO} \cdot \text{C(OH)} \end{array} \text{CH}$ , m. p. 247° (decomp.), is produced, which forms radiating prisms. By the action of chloroacetic acid on *2-thio-5-hydroxy-1-methyluracil*, *5-hydroxy-1-methyl-6-pyrimidone-2-thiolacetic acid*,  $\text{NMe} \begin{array}{c} \text{C(S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H)} : \text{N} \\ \text{CO} - \text{C(OH)} \end{array} \text{CH}$ , is obtained, which

forms stout prisms and decomposes at 217°.

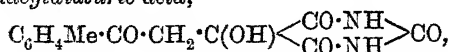
*5-Ethoxy-2-ethylthiol-3-methyl-6-pyrimidone*,



m. p. 149—151°, crystallises in small prisms, and combines with potassium iodide to form the compound,  $3\text{C}_9\text{H}_{14}\text{O}_2\text{N}_2\text{S}_2\text{KI}$ , which, on treatment with hydrochloric acid, yields *2-thio-5-ethoxy-3-methyl-6-pyrimidone*,  $\text{NH} \begin{array}{c} \text{CS} - \text{NMe} \\ \text{CO} \cdot \text{C(OEt)} \end{array} \text{CH}$ , m. p. 210—211°, which forms long needles. E. G.

**Condensation Products of Alloxan.** OTTO KÜHLING and B. SCHNEIDER (*Ber.*, 1909, 42, 1285—1296. Compare Kühling, *Abstr.*, 1908, i, 571).—In continuation of the study of the condensation of alloxan with aromatic ketones (*Abstr.*, 1905, i, 944), an account is given of the condensation of alloxan with *p*-methyl- and *p*-methoxyacetophenone, together with the preparation and properties of some new derivatives of ethoxyphenacyldialuric and phenacyldialuric acids.

*p*-Methylphenacyldialuric acid,

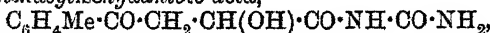


obtained in 78% yield by saturating an alcoholic solution of *p*-methylacetophenone and alloxan with hydrogen chloride at  $-7^\circ$ , crystallises from a mixture of acetone and water in white leaflets containing one molecule of solvent: m. p.  $241\text{--}242^\circ$  (decomp.); its sodium salt is a white, amorphous solid; its acetyl derivative forms leaflets, m. p.  $220^\circ$  (decomp.); the benzoyl derivative,  $\text{C}_{20}\text{H}_{16}\text{O}_6\text{N}_2$ , forms white prisms, m. p.  $215^\circ$  (decomp.).

*p*-Methylphenacyltartronic acid,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\begin{matrix} \diagup \text{C} \\ \diagdown \end{matrix}\begin{matrix} \text{OH} \\ \text{CO}_2\text{H} \end{matrix}$  is

obtained by warming *p*-methylphenacyldialuric acid with dilute aqueous sodium carbonate solution; it forms white aggregates of needles, which soften at  $139^\circ$ , m. p.  $158^\circ$  (decomp.); the lead salt,  $(\text{C}_{13}\text{H}_{13}\text{O}_6\text{N}_2)_2\text{Pb}$ , forms needle-shaped prisms.

*p*-Methylphenacylisoxydantonic acid,



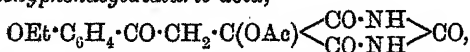
prepared by boiling *p*-methylphenacyltartronic acid in acetone, crystallises in white, prismatic leaflets, m. p.  $163\text{--}164^\circ$  (decomp.).

*p*-Methoxyphenacyldialuric acid,  $\text{C}_{13}\text{H}_{13}\text{O}_6\text{N}_2$ , from *p*-methoxyacetophenone and alloxan, forms white, prismatic leaflets, m. p.  $227^\circ$  (decomp.); its acetyl derivative forms white, rectangular leaflets, m. p.  $197^\circ$  (decomp.); benzoyl derivative, white, prismatic leaflets, m. p.  $240^\circ$  (decomp.).

*p*-Methoxyphenacyltartronic acid,  $\text{C}_{13}\text{H}_{14}\text{O}_7\text{N}_2$ , by action of sodium carbonate on *p*-methoxyphenacyldialuric acid, crystallises from a mixture of acetone and water or ether in aggregates of slender needles: m. p.  $144^\circ$  (slight decomp.), then becomes semi-solid, and decomposes completely at  $157^\circ$ ; the lead salt,  $(\text{C}_{13}\text{H}_{13}\text{O}_7\text{N}_2)_2\text{Pb}$ , forms white needles.

*p*-Methoxyphenacylisoxydantonic acid,  $\text{C}_{12}\text{H}_{14}\text{O}_6\text{N}_2$ , by heating the previous acid with acetone or by boiling an aqueous solution of *p*-methoxyphenacyldialuric acid, crystallises from acetone.

Acetyl-*p*-ethoxyphenacyldialuric acid,

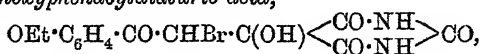


white, rectangular leaflets from aqueous acetone, m. p.  $207^\circ$  (decomp.); the corresponding benzoyl derivative forms white, prismatic leaflets from alcohol, m. p.  $224^\circ$  (decomp.).

*p*-Ethoxyphenacyltartronic acid,  $\text{C}_{14}\text{H}_{16}\text{O}_7\text{N}_2$ , separates from acetone in aggregates of white needles, m. p.  $134^\circ$ , and decomposes completely at  $157^\circ$ , like the corresponding methoxy-acid; its lead salt,  $(\text{C}_{14}\text{H}_{15}\text{O}_7\text{N}_2)_2\text{Pb}$ , is amorphous.

*p*-Ethoxyphenacylisohydantoic acid,  $C_{13}H_{16}O_5N_2$ , prepared from the preceding acid and acetone, forms columnar prisms from acetone, m. p. 162—163° (decomp.).

*Bromo-p*-ethoxyphenacyldialuric acid,

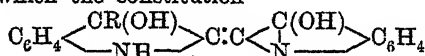


by action of bromine on a glacial acetic acid solution of *p*-ethoxyphenacyldialuric acid, separates from aqueous acetone in white, concentrically grouped needles, sinters at 171°, and decomposes at 201°; the *acetyl* derivative,  $C_{16}H_{15}O_7N_2Br$ , leaflets from aqueous alcohol, sinters at 165°, m. p. 178—179° (decomp.).

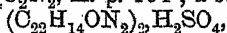
*Bromophenacyldialuric acid*,  $COPh \cdot CHBr \cdot C(OH) \begin{matrix} < CO \cdot NH > \\ < CO \cdot NH > \end{matrix} CO$ , prepared in similar manner, forms concentrically grouped needles, m. p. 217° (decomp.); the *silver* salt,  $C_{12}H_6O_5N_2BrAg$ , was analysed; the *acetyl* derivative,  $C_{14}H_{11}O_6N_2Br$ , forms rectangular prisms; it sinters at 181°, m. p. 194° (decomp.).

*Benzoylphenacyldialuric acid*,  $C_{19}H_{14}O_6N_2$ , prepared by benzoylating phenacyldialuric acid, forms prismatic needles from alcohol, m. p. 252° (decomp.). P. H.

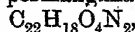
**Action of Grignard Reagents on Vat Dyes. I. Indigo.** FRANZ SACHS and HANS KANTOROWICZ (*Ber.*, 1909, 42, 1565—1576).—Synthetic indigotin dissolves readily in a large excess of ethereal organo-magnesium halide, yielding, after the usual treatment, substances to which the constitution



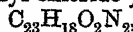
is ascribed, although the evidence is not conclusive; in some cases a small quantity of an acid is also produced. Magnesium methyl bromide yields a *substance*,  $C_{17}H_{14}O_2N_2$ , m. p. 209° (decomp.). Magnesium ethyl bromide yields a *substance*,  $C_{18}H_{16}O_2N_2$ , m. p. 245° (decomp.), which separates from alcohol in orange-coloured crystals, forms a *diethyl* derivative,  $C_{23}H_{24}O_2N_2$ , m. p. 95·5°, and is oxidised by potassium permanganate to the *substance*,  $C_{18}H_{16}O_2N_2(OH)_2$ , m. p. 111°. Magnesium propyl bromide yields the *substance*,  $C_{19}H_{18}O_2N_2$ , m. p. 222°. Magnesium isobutyl bromide yields the *substance*,  $C_{20}H_{20}O_2N_2$ , m. p. 220°. From magnesium isoamyl bromide are produced a red *substance*,  $C_{21}H_{22}O_2N_2$ , m. p. 211°, and a colourless *acid*, m. p. 148°, the *silver* salt of which,  $C_{21}H_{21}O_3N_2Ag$ , has m. p. 207° (decomp.). Magnesium phenyl bromide yields a colourless *acid*,  $C_{22}H_{16}O_3N_2$ , m. p. 228°, and a red *substance*,  $C_{23}H_{16}O_2N_2$ , m. p. 231°, which forms a *diethyl* derivative,  $C_{26}H_{24}O_2N_2$ , m. p. 104°, a *sulphate*,



and is oxidised by potassium permanganate to the *substance*,



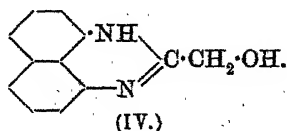
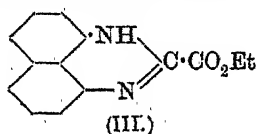
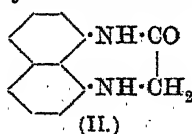
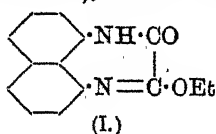
m. p. 198°. Magnesium benzyl chloride yields a *substance*,



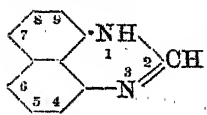
m. p. 182°. Magnesium *p*-tolyl bromide yield an *acid*, m. p. 223—230° (decomp.), and an orange-yellow *substance*,  $C_{23}H_{18}O_2N_2$ , m. p. 239° (decomp.). C. S.

Ring Formations in the Peri-Position of the Naphthalene Series. I. FRANZ SACHS [with BRUNO MYLO, GEORG MEYERHEIM, W. BRUNETTI, J. DAMM, H. MÖHRKE, M. SCHWABACHER, M. STEINER, and ARTHUR VOSS] (*Annalen*, 1909, 365, 53—166. Compare Kehrman and Engelke, this vol., i, 150).—A large number of important dyes have been prepared recently, in the formation of which a homo- or hetero-cyclic ring becomes attached to an anthracene molecule through the agency of one of the peri-positions (compare Bally, *Abstr.*, 1905, i, 237; *Farbenfabriken vorm. Friedr. Bayer & Co.*, *Abstr.*, 1908, i, 456). In order to gain some knowledge, therefore, of the part played by this type of ring formation in the production of dyes, the preparation and properties of compounds derived from naphthalene by condensation in the peri-position have been exhaustively studied. All the compounds described in this paper were prepared from 1:8-naphthylenediamine by condensation with monocarboxylic acids, oxalic acid, malonic acid, phthalic acid and other acids forming anhydrides, carbonic acid derivatives, substances containing sulphur, ketones, diketones, and ketocarboxylic acids.

It has been found impossible to build up seven-membered ring systems from 1:8-naphthylenediamine. In agreement with the view put forward by Hinsberg (*Abstr.*, 1889, 717), it is shown that the compounds investigated by Meyer and Müller (*Abstr.*, 1897, i, 356), to which formulæ were assigned containing seven-membered ring systems (I and II), have in reality the constitutional formulæ III and IV.



The parent compound of the substances described later is prepared by the action of formic acid on 1:8-naphthylenediamine, and has the annexed formula. This substance is designated perimidine; by this name attention is directed to the *peri*-position of the naphthalene nucleus and the *imidine*-like arrangement of the nitrogen atoms. The 2-methyl derivative is already known (Sachs, *Abstr.*, 1906, i, 829).



An interesting reaction occurs when a substituted acetoacetic ester is heated in aqueous solution with 1:8-naphthylenediamine hydrochloride; the Me·CO- group being eliminated from the ester to form 2-methylperimidine and replaced by hydrogen. It is thus possible by this method to prepare esters of the higher aliphatic acids; for example, ethyl propionate and ethyl  $\beta$ -phenylpropionate are obtained from ethyl ethylacetoacetate and ethyl benzylacetoacetate respectively.

As the result of this investigation, it is found, in agreement with

the statement made originally by Bamberger (Abstr., 1887, 495), that ring formation takes place more readily in the peri-position than in the ortho-position. Further, unlike the simple derivatives of *o*-phenylenediamine, such as phenyleneazoimide and benziminazole, which are colourless, the peri-derivatives are highly coloured provided an ethylene linking is present in the new ring. The simple members of the series are yellow, yellowish-green, orange, and red, but compounds having more intense and deeper colours are produced by nitration, reduction, etc. The dyes obtained in this manner are extremely fast, so that the presence of the peri-ring confers valuable dyeing properties on a compound.

I. 1:8-Naphthylenediamine and Monocarboxylic Acid.—Perimidine,  $C_{11}H_8N_2$ , obtained by the interaction of the diamine and formic acid, either alone or in alcoholic solution, or by heating the base with chloroform and calcium oxide at  $140^\circ$ , forms green crystals, m. p.  $222^\circ$ . The following salts were prepared and analysed: *hydrochloride*,  $C_{11}H_8N_2 \cdot HCl$ , yellowish-green needles, decomposing at  $300^\circ$ ; *nitrate*,  $C_{11}H_8N_2 \cdot HNO_3$ , long, green needles; *picrate*,  $C_{11}H_8N_2 \cdot C_6H_3O_7N_3$ , short, brownish-green needles, m. p.  $226^\circ$ ; *hydrogen sulphate*,

$C_{11}H_8N_2 \cdot H_2SO_4$ , crystals, decomposing slowly at  $300^\circ$ ; *sulphate*,  $(C_{11}H_8N_2)_2 \cdot H_2SO_4$ , decomposing at  $250^\circ$ ; *platinichloride*,  $C_{22}H_{16}N_4 \cdot H_2PtCl_6$ , pale yellow powder; *formate*,  $C_{11}H_8N_2 \cdot H \cdot CO_2H$ , m. p.  $143^\circ$ ; *acetate*,

$C_{11}H_8N_2 \cdot Me \cdot CO_2H$ , pale yellow, crystalline aggregates, m. p.  $130^\circ$ ; *oxalate*,

$C_{11}H_8N_2 \cdot C_2H_2O_4$ , yellow, crystalline powder, decomposing at  $270^\circ$ ; *malonate*,

$C_{11}H_8N_2 \cdot C_3H_4O_4$ , m. p.  $158^\circ$ ; *pyruvate*,  $C_{11}H_8N_2 \cdot C_3H_3O_3$ . Perimidine is converted by nitric acid (D 1.40) in glacial acetic acid into a vermilion *nitro*-derivative and a *dinitroperimidine*, crystallising in small, yellowish-brown needles. Perimidine couples with *p*-nitrodiazobenzene acetate, yielding *p*-nitrobenzeneazoperimidine,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CH}$ , obtained as blue crystals.

The following derivatives of 2-methylperimidine have been prepared: *hydrochloride*, yellow needles, which darken at  $300^\circ$  but do not melt; *nitrate*,  $C_{12}H_{10}N_2 \cdot HNO_3$ ; *acetate*, m. p.  $130$ – $140^\circ$ ; *oxalate*, m. p.  $232^\circ$ ; *picrate*, short, dark yellow needles, m. p.  $258^\circ$ ; *p*-nitrobenzeneazo-2-methylperimidine,  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CMe}$ , violet crystals, decomposing at  $165$ – $190^\circ$ ; *m*-nitrobenzeneazo-2-methylperimidine,  $C_{18}H_{13}O_2N_5$ , brownish-red crystals.

2-Ethylperimidine,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CEt}$ , obtained by the action of propionic anhydride on the diamine, crystallises in faintly yellow, felted needles, m. p.  $161^\circ$ ; the *hydrochloride*, long, silky needles, decomposing at  $220^\circ$ ; *sulphate*, yellow needles, m. p.  $199^\circ$ ; *oxalate*, fine yellow, crystalline powder, m. p.  $207^\circ$ ; *picrate*, orange-red, glistening precipitate, m. p.  $230^\circ$  (decomp.), and *acetate*, decomposing above  $260^\circ$ , were prepared.

2-Propylperimidine,  $C_{14}H_{14}N_2$ , crystallises in yellow, felted needles, m. p.  $157^\circ$ ; the *hydrochloride*, yellow needles, decomposing at  $240^\circ$ ; *sulphate*, m. p.  $232^\circ$ ; *picrate*, yellowish-brown, crystalline powder, m. p.  $220^\circ$  (decomp.); *oxalate*, yellow needles, m. p.  $222^\circ$ , and *nitrate*, golden-yellow, crystalline precipitate, decomposing at  $257^\circ$ , were prepared.

2-Phenylperimidine *hydrochloride* is obtained as yellow needles, decomposing at  $240^\circ$ , by the action of benzyl chloride on the diamine in benzene. The free base has m. p.  $187^\circ$  (compare Noetting, Abstr., 1902, i, 315). The *nitrate*, yellow powder, decomposing at  $180^\circ$ , and *picrate*, yellow needles, were prepared and analysed.

2-Benzylperimidine,  $C_{18}H_{14}N_2$ , prepared by the action of phenylacetyl chloride on the diamine, crystallises in slender, pale yellowish-green needles, m. p.  $194^\circ$ ; the *nitrate* forms yellow needles, m. p.  $238^\circ$ ; the *sulphate* forms golden-yellow needles, m. p.  $231^\circ$ ; the *hydrochloride* crystallises in yellow needles, and decomposes above  $180^\circ$ ; the *picrate* forms yellow needles, m. p. about  $210^\circ$ .

II. 1:8-Naphthylenediamine and Oxalic or Malonic Acid.—Oxalic acid interacts with the diamine in a variety of ways, depending on the conditions. In cold alcoholic solution they combine to form the *oxalate*,  $C_{10}H_{10}N_2 \cdot C_2H_2O_4 \cdot 2H_2O$ , obtained as a white precipitate decomposing at  $270^\circ$ ; under certain conditions, the *oxalate*,

( $C_{10}H_{10}N_2$ ) $_2 \cdot H_2C_2O_4$ , m. p.  $205^\circ$ , is obtained. Condensation between the diamine and oxalic acid takes place when an aqueous solution of the oxalate is boiled, resulting in the formation of perimidine-2-carboxylic acid. The latter substance is also formed when oxalic acid and the diamine are heated together at  $100$ — $140^\circ$ .

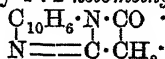
Ethyl perimidine-2-carboxylate,  $C_{10}H_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$ , is prepared by heating the diamine with ethyl oxalate (compare de Aguiar, this Journ., 1874, 699; Meyer and Müller, loc. cit.). Perimidine ethyl *oxalate*,  $C_{11}H_8N_2 \cdot \text{CO}_2\text{H} \cdot \text{CO}_2\text{Et}$ , is formed at the same time; it may also be prepared by treating perimidine in alcoholic solution with ethyl hydrogen oxalate, and crystallises in rosettes of straw-yellow crystals, m. p.  $204^\circ$ . Ethyl perimidine-2-carboxylate forms a *picrate*,

$C_{14}H_{12}O_2N_2 \cdot C_6H_3O_7N_3$ , obtained as dark violet crystals, m. p. above  $200^\circ$  (decomp.), and an *oxalate*, reddish-brown, fibrous crystals, m. p.  $248^\circ$ . It is converted by concentrated hydrochloric acid under pressure at  $140$ — $160^\circ$  into perimidine-2-carboxylic acid,  $C_{10}H_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ , obtained as golden, glistening scales decomposing above  $250^\circ$ . The *alkali* salts of the latter substance are unstable; the *hydrochloride*,  $C_{12}H_8O_2N_2 \cdot \text{HCl}$ , prepared by the action of dry hydrogen chloride on the acid suspended in glacial acetic acid, has an intense red colour. All attempts to prepare the chloride and amide of perimidine-2-carboxylic acid were unsuccessful; the *anilide*,  $C_{11}H_7N_2 \cdot \text{CO} \cdot \text{NHPh}$ , obtained by heating the ethyl ester and aniline together at  $160^\circ$ , forms bright red, nodular crystals, m. p.  $278^\circ$ . Ethyl perimidine-2-carboxylate, when heated with 1:8-naphthylenediamine at  $140$ — $150^\circ$ , yields 2:2-diperimidyl,

$C_{10}H_6 \begin{smallmatrix} < NH \\ < N \end{smallmatrix} > C \cdot C \begin{smallmatrix} < NH \\ < N \end{smallmatrix} > C_{10}H_6$ , obtained as dark red crystals, which do not melt at  $300^\circ$ . The ethyl ester is reduced by zinc dust and acetic acid, yielding 2-hydroxymethylperimidine,  $C_{11}H_7N_2 \cdot CH_2 \cdot OH$ , which crystallises in slender, greenish-yellow needles, m. p.  $221^\circ$ ; the latter substance may be synthesised by heating 1:8-naphthylenediamine with glycollic acid or chloroacetic acid. The following derivatives of the ethyl ester were also prepared and analysed: *acetate*, lemon-yellow powder, m. p.  $130-140^\circ$  (decomp.); *picrate*, long, glistening, yellow lamellæ, decomposing at  $230-240^\circ$ ; *oxalate*, yellow crystals, m. p.  $223^\circ$ ; *malonate*, and *nitrate*.

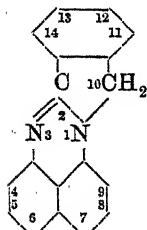
*Methyl perimidine-2-carboxylate*,  $C_{11}H_7N_2 \cdot CO_2Me$ , prepared from the diamine and methyl oxalate, crystallises in aggregates of long, red needles, m. p.  $197^\circ$ .

1:8-Naphthylenediamine, when heated with malonic acid at  $100-150^\circ$ , yields 2-methylperimidine, malonate and a substance crystallising in small scales with a silvery-grey lustre, m. p.  $210^\circ$  (decomp.), which is probably 1:2-ketomethyleneperimidine,



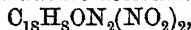
*Ethyl perimidylacetate*,  $C_{11}H_7N_2 \cdot CH_2 \cdot CO_2Et$ , is obtained when the diamine is boiled with ethyl malonate; it forms sulphur-yellow crystals, m. p.  $152^\circ$ ; a substance (C=73.75, H=5.25, N=12.75) is obtained at the same time as a pale yellow powder. *Methyl perimidylacetate*,  $C_{14}H_{12}O_2N_2$ , prepared in a similar manner, has m. p.  $184^\circ$ .

III. 1:8-Naphthylenediamine with Phthalic Acid and other Dicarboxylic Acids which form Anhydrides.—The parent substance of the compounds described in this division is designated *phthaloperine*, and has the annexed formula. A 100%

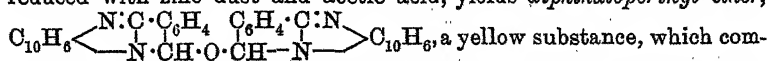


yield of 10-phthaloperinone,  $C_{18}H_8 \cdot C \cdot N$ , is obtained

when the diamine is heated with phthalic anhydride at  $150-230^\circ$ ; it sublimes, forming stellate groups of long, soft, scarlet needles, m. p.  $229-230^\circ$  (corr.). It is converted by concentrated nitric acid at the ordinary temperature into a *dinitro*-derivative,



which crystallises in red needles, m. p.  $247^\circ$ , and is reduced by ammonium sulphide to the corresponding *diamino*-derivative,  $C_{18}H_8ON_2(NH_2)_2$ , red crystals, m. p.  $255-260^\circ$ . *Dibromophthaloperinone*,  $C_{18}H_8ON_2Br_2$ , obtained by the action of bromine in acetic acid on phthaloperinone, crystallises in small, slender, red needles, and decomposes at  $240^\circ$ . Phthaloperinone, when reduced with zinc dust and acetic acid, yields *diphthaloperinyl ether*,



a yellow substance, which commences to decompose at a red heat. Phthaloperinone reacts with magnesium methyl iodide, yielding 10-hydroxy-10-methylphthaloperine,  $C_{19}H_{14}ON_2$ , which crystallises in olive-brown rhombohedra, m. p.  $241^\circ$ ;

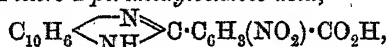
the *hydriodide*,  $C_{19}H_{14}ON_2 \cdot HI$ , is red; the *picrate* is a brownish-red powder.

The following compounds are obtained by similar methods: 10-*hydroxy-10-ethylphthaloperine*,  $C_{20}H_{16}ON_2$ , olive-brown crystals, m. p.  $243^\circ$ ; 10-*hydroxy-10-phenylphthaloperine*,  $C_{24}H_{16}ON_2$ , brown crystals, m. p.  $282-284^\circ$ ; the *hydrochloride*,  $C_{24}H_{16}ON_2 \cdot HCl$ , crystallises in brown prisms; 10-*hydroxy-10-benzylphthaloperine*,  $C_{25}H_{18}ON_2$ , crystallises in rhombohedra, m. p.  $258-259^\circ$ , and, when boiled with acetic anhydride, yields 10-*benzylidenephthaloperine*,  $C_{25}H_{16}N_2$ , crystallising in purplish-red nodules, m. p.  $191^\circ$ .

*o-Perimidylbenzoic acid*,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{NH} \end{smallmatrix} \text{C} \cdot C_6H_4 \cdot CO_2H$ , is formed when the condensation of phthalic anhydride with 1:8-naphthylenediamine is carried out in various solvents; also when phthaloperinone is heated with concentrated hydrochloric acid. It is obtained as yellow flakes, and does not possess a definite m. p.

11-(or 14-)*Nitro-10-phthaloperinone*,  $C_{18}H_9O_3N_3$ , prepared by heating the diamine with 3-nitrophthalic acid at  $185-200^\circ$ , forms dark red crystals, m. p.  $210-215^\circ$ . 12-(or 13-)*Nitro-10-phthaloperinone*,

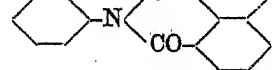
$C_{18}H_9O_3N_3$ , prepared similarly by using 4-nitrophthalic acid, forms red crystals, m. p.  $278-280^\circ$ ; the acid anhydride and the diamine unite in ethereal solution, yielding 4-*nitro-2-perimidylbenzoic acid*,



a pale brick-red powder, which loses water at  $205^\circ$  and passes into the anhydro-derivative.

*Dichlorophthaloperinone*,  $C_{18}H_8ON_2Cl_2$ , prepared by heating dichlorophthalic acid with the diamine, has m. p.  $235-237^\circ$ ; it yields a *dibromo*-derivative,  $C_{18}H_8ON_2Cl_2Br_2$ , reddish-violet crystals, m. p.  $224^\circ$ , and a *dinitro*-derivative,  $C_{18}H_8O_5N_4Cl_2$ , a yellowish-brown substance decomposing at  $213-215^\circ$ . Dichlorophthalic anhydride and the diamine combine in ethereal solution, yielding *perimidyl-dichlorobenzoic acid*,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{NH} \end{smallmatrix} \text{C} \cdot C_6H_2Cl_2 \cdot CO_2H$ , yellowish-red crystals, which lose water at  $180^\circ$ .

*Naphthaloperinone*, annexed formula, prepared by heating the diamine with naphthalic anhydride at  $180-200^\circ$ , forms long, dark red crystals, m. p.  $253^\circ$ ; the *dinitro*-derivative,

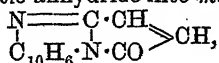


$C_{22}H_{10}O_5N_4$ , forms red crystals, decomposing at  $300-310^\circ$ ; the *diamino*-derivative,  $C_{22}H_{14}ON_4$ , is a bluish-violet powder, decomposing above  $300^\circ$ ; the *dibromo*-derivative,  $C_{22}H_{10}ON_2Br_2$ , crystallises in nodules of red needles, m. p.  $261^\circ$ . The parent substance is converted by alcoholic potassium hydroxide into 8-*perimidyl-naphthoic acid*,  $C_{11}H_7N_2 \cdot C_{10}H_6 \cdot CO_2H$ , a brown substance, which passes into the anhydride at  $180^\circ$ .

Succinic anhydride and 1:8-naphthylenediamine interact in toluene, yielding *perimidylpropionic acid*,  $C_{11}H_7N_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , a yellowish.

grey substance, m. p. 253°, which, when heated at this temperature, passes into *succinoperinone*,  $\text{C}_{10}\text{H}_6 \cdot \text{N} \cdot \text{CO} \begin{array}{c} \text{N}=\text{C} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$ , m. p. 158°.

*Perimidylacrylic acid*,  $\text{C}_{11}\text{H}_7\text{N}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , is obtained as a brownish-red precipitate, decomposing at 210°, by the action of maleic anhydride on 1:8-naphthylenediamine in glacial acetic acid; it is converted by boiling acetic anhydride into *maleinoperinone*,



m. p. 161°.

IV. 1:8-Naphthylenediamine and Carbonic Acid Derivatives.—*Dihydro-2-perimidone* (1:8-naphthylenecarbamide),



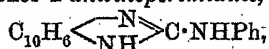
may be prepared by the action of carbonyl chloride, ethyl chloro-carbonate, ethyl carbonate, or hydrocyanic acid on the diamine; it forms glistening, white crystals, m. p. 304—305°. *2-Ethoxyperimidine*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{COEt}$ , is obtained by heating the diamine with ethyl orthocarbonate at 140—180°; it crystallises in almost colourless needles, m. p. 125°, and is converted by hot concentrated hydrochloric acid into the dihydroperimidone just described; the *hydrochloride*,  $\text{C}_{10}\text{H}_{12}\text{ON}_2 \cdot \text{HCl}$ , forms white crystals, decomposing at 300°; the *sulphate* crystallises in white needles, m. p. 192°. Dihydro-2-perimidone, when heated with phosphoryl chloride under pressure at 130°, yields *2-chloroperimidine*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{CCl}$ , crystallising in greyish-green leaflets, m. p. 194°. *2-Thiodihydroperimidone*,



prepared by acting on the diamine with carbon disulphide or potassium xanthate, crystallises in large, glistening leaflets, which sublime without melting.

V. 1:8-Naphthylenediamine with Compounds containing Sulphur or Selenium.—*2-Aminoperimidine*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C} \cdot \text{NH}_2$ , formed together with the dihydrothioperimidone just described by the action of ammonium thiocyanate on the diamine, is a yellowish-white substance, m. p. 239°; the *sulphate*, *acetate*, *nitrate*, *hydrochloride*, m. p. 282°, *picrate*, red leaflets, and *platinichloride* were prepared.

*Phenyl-8-aminonaphthylthiocarbamide*,  $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ , prepared by acting on the diamine with phenylthiocarbimide in cold benzene, is a yellowish-white substance, m. p. 238°. When the solution of these components in benzene is boiled for twelve hours, a substance is obtained which is either *2-anilinoperimidine*,

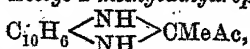


or *phenyl-1:8-naphthyleneguanidine*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C} \cdot \text{NPh}$ ; it crystallises in glistening, white leaflets, m. p. 245°; the *picrate* is red.

The following compounds are prepared by similar methods: *o*-Tolyl-8-aminonaphthylthiocarbamide,  $C_7H_7 \cdot NH \cdot CS \cdot NH \cdot C_{10}H_6 \cdot NH_2$ , an almost white substance, m. p.  $229^\circ$ ; 2-*o*-toluidinoperimidine,  $C_{18}H_{15}N_3$ , m. p.  $240-241^\circ$ . *p*-Tolyl-8-aminonaphthylthiocarbamide,  $C_{18}H_{17}N_3S$ , m. p.  $259^\circ$ ; 2-*p*-toluidinoperimidine,  $C_{18}H_{15}N_3$ , m. p.  $247^\circ$ . Allyl-8-aminonaphthylthiocarbamide,  $C_{14}H_{15}N_3S$ , yellowish-white needles, which commence to decompose at  $170^\circ$ , m. p.  $300^\circ$ ; allyl-8-aminonaphthylcarbamide,  $C_{14}H_{15}ON_3$ , is obtained by treating an alcoholic solution of the latter substance with mercuric oxide; it has m. p.  $225^\circ$ . Phenyl-8-aminonaphthylcarbamide,  $C_{17}H_{15}ON_3$ , crystallises in white leaflets with a red tinge, m. p.  $304^\circ$ .

Thionyl chloride, when boiled with a solution of the diamine in benzene, yields a substance having the formula  $C_{10}H_6 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle SO$  or  $C_{10}H_6 \langle \begin{smallmatrix} N \\ N \end{smallmatrix} \rangle S \cdot H_2O$ . Selenious acid reacts with the diamine dissolved in 50% acetic acid, yielding a substance,  $C_{10}H_6 \langle \begin{smallmatrix} N \\ N \end{smallmatrix} \rangle Se$ , obtained as a black, infusible precipitate.

VI. Action of Ketones, Diketones, and Ketocarboxylic Acids on 1:8-Naphthylenediamine.—2-Acetyl-2-methyldihydroperimidine,



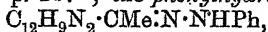
is prepared by acting on the diamine with diacetyl in alcoholic solution, and forms colourless crystals, m. p.  $181-183^\circ$ ; the phenylhydrazone,  $C_{12}H_{11}N_2 \cdot CMe \cdot N \cdot NHPh$ , crystallises in white, fan-shaped needles, sinters at  $145^\circ$ , m. p.  $147-149^\circ$ ; the oxime,  $C_{12}H_{11}N_2 \cdot CMe \cdot NOH$ , crystallises in yellow needles decomposing at about  $300^\circ$ ; the semicarbazone,  $C_{12}H_{11}N_2 \cdot CMe \cdot N \cdot NH \cdot CO \cdot NH_2$ , has m. p.  $224-226^\circ$ ; the azine,  $(C_{12}H_{11}N_2 \cdot CMe)_2N_2$ , forms pink crystals, m. p.  $229^\circ$  (decomp.); the benzylidene derivative,  $C_{12}H_{11}N_2 \cdot CO \cdot CH : CHPh$ , is obtained as the hydrochloride by acting on a solution of the perimidine in alcohol with benzaldehyde in the presence of hydrogen chloride; the hydrochloride is a brownish-yellow powder without a sharp m. p.

1:8-Naphthylenediamine condenses with isatin, forming a substance,  $C_{10}H_6 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle C \langle \begin{smallmatrix} CO \\ C_6H_4 \end{smallmatrix} \rangle NH$ , which sinters at  $170^\circ$ , m. p.  $181^\circ$ , and, when heated further, yields another substance, crystallising in long needles, m. p.  $254^\circ$ . The condensation product of the diamine with alloxan has the formula  $C_{10}H_6 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle C \langle \begin{smallmatrix} CO \cdot NH \\ CO \cdot NH \end{smallmatrix} \rangle CO$ ; it crystallises in slender, white needles.

Ethyl acetoacetate reacts with the diamine at the ordinary temperature with the formation of ethyl 2-methyldihydroperimidylacetate,  $C_{10}H_6 \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \rangle CMe \cdot CH_2 \cdot CO_2Et$ , white, glistening needles, m. p.  $97^\circ$ ; the sulphate, yellow needles decomposing above  $260^\circ$ , and oxalate, m. p.  $241^\circ$ , were prepared. The substance decomposes when heated at  $150-160^\circ$ , yielding ethyl acetate and 2-methylperimidine.

Acetonylperimidine,  $C_{10}H_6 \langle \begin{smallmatrix} N \\ NH \end{smallmatrix} \rangle C \cdot CH_2 \cdot COMe$ , is formed when

the diamine is boiled with ethyl acetoacetate; it crystallises in glistening, yellow needles, m. p. 267°; the *phenylhydrazone*,



forms yellow crystals, m. p. 195°. When the same substances are heated together with dilute hydrochloric acid, they interact, yielding ethyl acetate and 2-methylperimidine.

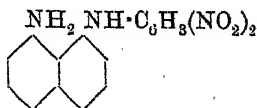
Methyl acetoacetate reacts in the same manner with the diamine; *methyl 2-methyldihydroperimidylacetate*,  $\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2$ , crystallises in glistening, white needles, m. p. 145°. *Ethyl 2-methyldihydroperimidylpropionate*,  $\text{C}_{10}\text{H}_8\text{N}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , prepared from the diamine and ethyl laevulate, crystallises in white needles, m. p. 102°.

1:8-Naphthylenediamine (1 mol.) reacts with acetylacetone (1 mol.), yielding 2-methylperimidine and acetone; 2:2-dimethyldihydroperimidine,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CMe}_2$ , long needles, m. p. 117°, is also formed

when an excess of the diketone is employed. Benzoylacetone (1 mol.) reacts with the diamine (1 mol.), yielding at first 2-methylperimidine and acetophenone; the latter substance interacts with another molecule of the diamine, yielding 2-phenyl-2-methyldihydroperimidine,  $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CMePh}$ , obtained as a white precipitate.

Benzenesulphonyl chloride reacts with the diamine dissolved in benzene in the presence of potassium carbonate, yielding *dibenzenesulphonyl-1:8-naphthylenediamine*,  $\text{C}_{22}\text{H}_{18}\text{O}_4\text{N}_2\text{S}_2$ , m. p. 192.5°, which couples with diazobenzenesulphonic acid in alkaline solution, forming an *azo-dye*; the latter substance when reduced yields *dibenzenesulphonyl-1:4:8-triaminonaphthalene*,  $\text{C}_{22}\text{H}_{19}\text{O}_4\text{N}_3\text{S}_2$ , a white, crystalline substance, m. p. 200° (decomp.).

2':4-Dinitro-8-aminophenyl-naphthylamine, annexed formula, prepared by boiling the diamine with chlorodinitrobenzene in alcoholic solution in the presence of sodium acetate, forms red crystals, m. p. 203.5—204°.



W. H. G.

Reduction of *cycloAmine-ones*. II. Diacridyl. HERMAN DECKER and GEORGES DUNANT (*Ber.*, 1909, 42, 1176—1178).—By the reduction of 10-methylacridone (*Abstr.*, 1906, i, 901) a yellow precipitate is obtained in addition to methylacridonium hydroxide and methyldihydroacridine. This yellow compound is regarded as dimethyldiacridine,  $\text{NMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{NMe}$ , and the crystalline product obtained by the action of nitric acid as *dimethyldiacridylum nitrate*,  $\text{NO}_3 \cdot \text{NMe} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{NMe} \cdot \text{NO}_2$ . This nitrate forms large, glistening plates, only sparingly soluble in hot water, and is not molten at 330°. When reduced with zinc dust and acetic acid, it yields 10-methylacridonium hydroxide. Solutions of the salt do not yield precipitates with sodium hydroxide solution, but give precipitates with solutions of other salts. The *chromate* is a crystalline, yellow precipitate; the *sulphate* forms sparingly soluble, yellow

crystals; the *picrate*,  $C_{40}H_{26}O_{14}N_8$ , crystallises from alcohol in yellow crystals, m. p.  $300^\circ$  (decomp.); and the *iodide* forms glistening, red crystals, which lose methyl iodide readily at  $245\text{--}270^\circ$ , yielding

*diacridyl*,  $N \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} C \cdot C \begin{array}{c} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} N$ , as a colourless, crystalline base, m. p. above  $350^\circ$ .

J. J. S.

**Question of the Attachment of the Purine Bases in the Nucleic Acid Molecule.** HANS FISCHER (*Zeitsch. physiol. Chem.*, 1909, 60, 69—78).—According to Burian (Abstr., 1904, i, 354), purine bases and iminazoles which are not substituted in position 7 react with diazobenzenesulphonic acid, yielding coloured compounds, which were regarded as diazoamino-compounds. The products of reduction of these coloured compounds indicate that the compounds are azo-dyes with the  $\cdot N:NR$  group attached to carbon number 8.

Theophylline combines with *p*-dichlorodiazobenzene chloride, yielding a dye which crystallises from alcohol or acetic acid in brilliant red needles. When reduced with sodium hyposulphite, it yields 8-aminotheophylline (compare D.R.-P. 156900) and dichloro-aniline. The same aminotheophylline is obtained when Burian's theophylline diazobenzenesulphonate is reduced. It can be diazotised, and then forms dyes with R-salt, but it does not combine with diazo-compounds.

Xanthine reacts with *p*-dichlorodiazobenzene chloride, yielding a brownish-red dye, which gives 8-aminoxanthine when reduced. This amino-compound can be diazotised, and yields the *anhydro*-compound,

$CO \begin{array}{c} \diagup NH \cdot CO \cdot C \cdot N \cdot N \\ \diagdown NH \cdot C \cdot N : C \cdot N \end{array}$ , which crystallises in yellow masses of needles

similar to tyrosine. It explodes at  $150^\circ$ , couples with an alkaline solution of R-salt, and when evaporated to dryness several times with 20% hydrochloric acid yields uric acid.

Guanine and *p*-dichlorodiazobenzene chloride yield a dark red dye, which forms 8-aminoguanine (2:8-diamino-6-pyrimidone) when reduced. 8-Aminoguanine sulphate,  $2C_5H_7ON_6 \cdot H_2SO_4 \cdot 2H_2O$ , crystallises in long needles, and loses its water of hydration at  $120\text{--}130^\circ$ . The amino-compound does not couple with diazo-compounds, but can be diazotised itself at  $40^\circ$ , and then reacts with an alkaline solution of R-salt, yielding a violet dye.

The conclusion is drawn that in nucleic acids the phosphorus atom is attached to the purine bases in positions 7 or 8 (compare Burian, Abstr., 1904, i, 358).

J. J. S.

**Physico-chemical and Chemical Investigations on the Behaviour of Uric Acid in Solution.** F. GUDZENT (*Zeitsch. physiol. Chem.*, 1909, 60, 25—37. Compare His and Paul, Abstr., 1900, i, 591; Gudzent, Abstr., 1908, i, 704).—The following constants have been determined for uric acid at  $37^\circ$ . Solubility in water, 1 in 15,505 parts, or 1 litre of solution contains 0.0649 gram of acid. Specific electrical conductivity, 0.000013, and molecular conductivity, 33.92. Degree of ionisation of saturated solution, 0.075. Dissociation constant,  $K = 0.000233$ . Heat of solution,  $-8954$  cal.

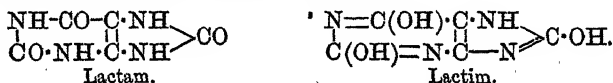
When shaken with water, uric acid decomposes, so that the solubility tends to increase with the time. The increase is only noticed at the end of twenty-four hours, and then rises rapidly, so that at the end of ten days the solubility is eleven times as great as at the end of a few hours, and in the same time the electrical conductivity of the solution has increased some fifty-five times.

An increase in the electrical conductivity is also observed when a saturated solution of the acid is kept in the absence of solid uric acid. Platinum has an accelerating effect on this change, and the curves obtained by plotting the conductivities against the time show that the reaction has a logarithmic course, indicating that a state of equilibrium is reached.

J. J. S.

**Physico-chemical Researches on the Behaviour of Urates in Solution.** F. GUDZENT (*Zeitsch. physiol. Chem.*, 1909, 60, 38—68. Compare Abstr., 1908, i, 704).—As the result of a series of investigations, the following conclusions are drawn.

(1) Uric acid forms two series of primary metallic salts (monosodium, potassium, and ammonium urates), which differ as regards solubility. The salts of the *a*-series cannot be obtained pure, as at the moment of their formation in water they tend to pass over into salts of the *b*-series. The probable cause of this change is an intramolecular rearrangement, so that the two series correspond with the two tautomeric forms of uric acid:



The unstable *a*-series are probably lactam urates, and the stable *b*-series, lactim urates.

(2) The *a*-salts have solubilities and specific conductivities which at 18° are some 33·4%, or at 37° 33·9%, greater than the corresponding values for the more stable *b*-salts.

(3) The transformation is practically complete, and the velocity of transformation is rapid in a homogeneous system, but much slower in a heterogeneous system, and depends on the amount of solid and of solvent present.

(4) The following constants at 18° and 37° are given in the original for the *a*- and *b*-modifications of the monosodium, monopotassium, and monoammonium salts, and also for mixtures of the two forms such as are usually met with in the ordinary commercial preparations of urates: solubility, molecular conductivity, conductivity at  $v_{\infty}$ , migration values of the anions, time required to obtain a saturated solution, concentration of free hydroxyl ions, and degree of hydrolysis.

(5) The *a*- and *b*-forms of any one salt appear to be isomorphous.

J. J. S.

**Isomeric Azoxy-compounds.** ARNOLD REISSERT (*Ber.*, 1909, 42, 1364—1371).—Up to the present time no cases of isomeric azoxy-compounds have been observed in which the isomerism is undoubtedly due to a constitutional or steric difference in the azoxy-

groups (compare Janovsky and Reimann, Abstr., 1889, 392, 865; Bamberger, Abstr., 1900, i, 531; 1902, i, 505; Kekulé and Hidegh, *Ber.*, 1870, 3, 235).

On treating nitrosobenzene at low temperatures with aqueous-alcoholic sodium hydroxide, instead of alcoholic potassium hydroxide (compare Bamberger, Abstr., 1902, i, 279), the author obtains the known azoxybenzene together with a small quantity of an isomeric compound, to which he gives the name *iso*azoxybenzene; similarly, *o*-nitrosotoluene yields *o*-azoxytoluene and *o*-*iso*azoxytoluene, the latter in this case forming the main product. *p*-Nitrosotoluene yields *p*-azoxytoluene, together with a substance of high and indefinite m. p., which is evidently not a simple azoxy-compound. In the condensation of  $\beta$ -phenylhydroxylamine with nitrosobenzene, no trace of *iso*azoxybenzene is formed.

The two *iso*azoxy-compounds obtained are almost colourless, and when heated pass into the isomeric azoxy-compounds, the transformation not taking place at any definite temperature, but increasing in velocity as the temperature is raised. They are stable compounds, but a small quantity of bromine added to a chloroform solution of *iso*azoxytoluene converts the latter into azoxytoluene, probably by way of an intermediate additive bromine derivative (compare Wohl, Abstr., 1904, i, 201).

No specific chemical difference has been demonstrated between the isomeric azoxy-compounds. Phenylhydrazine acts on neither of the azoxytoluenes, whilst hydroxylamine converts the *iso*-compound partly into the normal form.

*iso*Azoxybenzene,  $C_6H_5 \cdot N_2O \cdot C_6H_5$ , crystallises from aqueous-methyl alcohol in slender needles, m. p.  $84^\circ$  if rapidly heated; if slowly heated, the compound begins to liquefy at  $81^\circ$ , at which temperature gradual change into azoxybenzene takes place.

*o*-*iso*Azoxytoluene,  $C_7H_7 \cdot N_2O \cdot C_7H_7$ , separates from light petroleum in faintly yellow, spear-like crystals, from aqueous methyl alcohol in needles, and from benzene in compact prisms, m. p.  $82^\circ$  (rapid),  $80-81^\circ$  (slow heating).

*Bromo-o*-azoxytoluene,  $C_7H_6Br \cdot N_2O \cdot C_7H_7$ , prepared from *o*-azoxytoluene or *o*-*iso*azoxytoluene, crystallises from 96% alcohol in almost colourless needles, m. p.  $68.5^\circ$ ; it is a derivative of *o*-azoxytoluene and not of the *iso*-compound, since the latter is converted into its isomeride by bromine (*vide supra*).

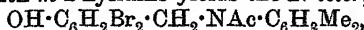
The substance,  $C_{21}H_{19}O_2N_3$  ( $= 3C_7H_7ON - H_2O$ ), obtained together with *p*-azoxytoluene by the action of aqueous-alcoholic sodium hydroxide on *p*-nitrosotoluene, liquefies at  $183-190^\circ$ , but the liquid becomes clear only at about  $250^\circ$ .

T. H. P.

**Influence of Substituents on the Capacity for Migration of Acid Residues.** KARL AUWERS (*Annalen*, 1909, 365, 278-290).—A continuation of the investigation on the intramolecular transformations of acylated compounds (this vol., i, 222). The results obtained by the author in conjunction with Hirt, von Heyden, Hannemann, and Dannehl are discussed fully in this paper (compare following abstracts).

The migration of the acid radicle is not prevented by the presence of

two ortho-substituents, since 3:5-dibromo-2-acetoxybenzyl bromide when condensed with *m*-2-xylydine yields the *N*-ester,



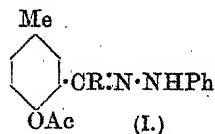
crystallising in needles.

The reduction of a very large number of derivatives of benzeneazo-*p*-tolyl acetate has been studied, and it is found that the migration of the acetyl group which takes place with the parent substance is totally prevented by the introduction of the most varied groups into the molecule with but one remarkable exception; the introduction of a methyl group in the para-position does not hinder the migration of the acid radicle (compare Auwers, Abstr., 1908, i, 228).

The introduction of various groups in the phenylhydrazine residue has a great influence on the capacity for migration of the acyl group in the *O*-acetates and *O*-benzoates of the substituted phenylhydrazones of salicylaldehyde.

The *O*-acetates and *O*-benzoates of the condensation products of salicylaldehyde with phenylhydrazine, *o*-tolylhydrazine, *o*-anisylhydrazine, *p*-chlorophenylhydrazine, *p*-bromophenylhydrazine, and *m*-2-xylylhydrazine, when heated with glacial acetic acid, pass into the isomeric *N*-acyl derivatives. The acetates, but not the benzoates, of the derivatives of *o*-chlorophenylhydrazine, *o*-bromophenylhydrazine, and *m*-nitrophenylhydrazine undergo the same transformation. Neither the acetates nor the benzoates undergo rearrangement when *o*-nitrophenylhydrazine and *p*-nitrophenylhydrazine are condensed with salicylaldehyde. It is evident, therefore, that the chemical nature of the substituent has a great influence on the stability of the hydrazone. The nitro-group is the only group of those investigated which is capable of preventing the migration of the acetyl group, and only then when in the ortho- or para-position to the imino-group; in the meta-position it only prevents the wandering of the heavier benzoyl group. Chlorine and bromine in the ortho-position also prevent the migration of the benzoyl group, but not when they occupy the para-position.

In the cases just cited it is evident that the steric, as compared with the chemical, influence of the ortho-substituents is quite negligible. However, steric influences have been detected in the intramolecular



transformations of the *O*-esters of the phenylhydrazones of *o*-hydroxy-ketones. The migration of the acyl group in compounds of type (I) does not occur when *R* represents a phenyl group, but does so when *R* is either hydrogen or methyl.

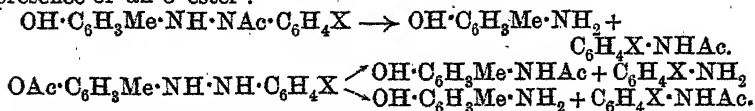
In this connexion, it is also found that the imino-hydrogen atom in phenylhydrazones of the type  $\text{CPhR}\cdot\text{N}\cdot\text{NHPh}$  is replaced only with great difficulty and occasionally not at all by acid radicles when *R* is a heavy group. Even the phenylhydrazones of benzophenone and acetophenone may be obtained unchanged after boiling for some time with acetic anhydride, whereas the hydrazone derivatives of salicylaldehyde and its substituted products are, generally speaking, acetylated with great readiness.

The same difference is encountered in the condensation of various aldehydes and ketones with *as*-phenylhydrazines. Aldehydes, likewise acetophenone and its derivatives, condense readily with *as*-acylphenyl-

hydrazines, whilst benzophenone and many of its derivatives do not yield condensation products with the same *as*-phenylhydrazine.

W. H. G.

**Acylated *o*-Hydroxyazo-substances and Their Reduction.** KARL AUWERS [with W. HIRT and FRIEDRICH VON DER HEYDEN] (*Annalen*, 1909, 365, 291—313. Compare preceding abstract).—The hydroxyazo-compounds described later were prepared by coupling the phenol with the diazo-salt in very dilute aqueous solution. The acetates were obtained by heating the hydroxyazo-compound with acetic anhydride and sodium acetate. The reduction of the acetyl derivatives to the corresponding hydrazo-compounds was accomplished by means of zinc dust and acetic acid, less frequently by sodium amalgam and acetic acid. The position of the acyl group in the molecule was determined by reducing the compound and testing the products formed for the free base,  $C_6H_4X \cdot NH_2$ , the isolation of which indicated the presence of an *O*-ester:



The following are the new compounds described:

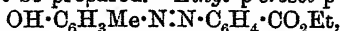
3-Benzeneazo-*m*-4-xenol,  $C_{14}H_{14}ON_2$ , glistening, dark red needles, m. p. 90° (compare Grevingk, *Abstr.*, 1886, 348); the *acetate*,  $C_{16}H_{16}O_2N_2$ , crystallises in bright red, glistening needles, m. p. 68°; *O*-acetylbenzenehydrazo-*m*-4-xenol,  $C_{16}H_{16}O_2N_2$ , is obtained as a pale yellow powder, m. p. 103°.

3-Benzeneazo-*o*-4-xenol crystallises in glistening, dark orange-red needles, m. p. 130°; the *acetate* forms orange-yellow, pearly leaflets, m. p. 113°; *O*-acetylbenzenehydrazo-*o*-4-xenol has m. p. 84—85°. Benzene-

azocresol,  $\begin{matrix} CH & - & CMe & = & CH \\ | & & & & | \\ C(OMe) \cdot C(OH) : C : N : NPh \end{matrix}$ , crystallises in red leaflets, m. p. 112°; the *acetate* crystallises in slender, glistening, red needles, m. p. 114°; the corresponding *O*-acetylhydrazo-derivative forms white leaflets, m. p. 102°; *O*-acetyl-3-benzenehydrazo-5-bromo-*p*-cresol,  $C_{15}H_{15}O_2N_2Br$ , forms slender, white leaflets, m. p. 91°.

3-*o*-Tolueneazo-*p*-tolyl *acetate*,  $C_{16}H_{16}O_2N_2$ , crystallises in small, red needles, m. p. 59°; the *O*-acetylhydrazo-compound,  $C_{16}H_{16}O_2N_2$ , forms white leaflets, m. p. 89°. 3-*m*-Tolueneazo-*p*-tolyl *acetate* forms compact, dark red crystals, m. p. 61—63°; the *O*-acetylhydrazo-compound crystallises in colourless leaflets, m. p. 92—95°. *N*-Acetyl-3-*p*-toluenehydrazo-*p*-cresol,  $C_{16}H_{16}O_2N_2$ , prepared by reducing 3-*p*-tolueneazo-*p*-tolyl *acetate* with sodium amalgam (compare Goldschmidt and Pollak, *Abstr.*, 1892, 974), crystallises in white leaflets, m. p. 102°. 4-*Xyleneazo-p*-cresol,  $C_{15}H_{16}ON_2$ , is a brownish-yellow, crystalline powder, m. p. 131—132°; the *acetate*,  $C_{17}H_{18}O_2N_2$ , crystallises in orange-yellow leaflets and flat needles, m. p. 106—106·5°, and when reduced yields the *O*-acetylhydrazo-compound. *p*-Anisylazo-*p*-cresol,  $C_{14}H_{14}O_2N_2$ , crystallises in small, red needles, m. p. 94—95°; the *acetate*,  $C_{16}H_{16}O_3N_2$ , forms slender, yellowish-red, felted needles, m. p. 60—61°; the corresponding *N*-acetyl-*O*-benzoate,  $C_{22}H_{19}O_2N_2Cl$ , forms slender, white, felted needles, m. p. 175—176°. *p*-Nitrobenzeneazo-*p*-tolyl *acetate*,  $C_{15}H_{13}O_4N_3$ ,

crystallises in slender, felted, red needles, m. p.  $184^{\circ}$ ; the hydrazo-compound could not be prepared. *Ethyl p-cresol-p-azobenzoate*,



forms small, red leaflets, m. p.  $96-97^{\circ}$ ; the *acetate* forms red leaflets, m. p.  $81^{\circ}$ ; the *O-acetylhydrazo*-compound,  $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$ , forms white leaflets, m. p.  $118-119^{\circ}$ .

*a-Naphthaleneazo-p-cresol*,  $\text{C}_{17}\text{H}_{14}\text{ON}_2$ , forms small, brownish-violet crystals, m. p.  $102-104^{\circ}$ ; the *acetate* is a light red, crystalline powder, m. p.  $109-111^{\circ}$ ; the *O-acetylhydrazo*-derivative,  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2$ , is a brown, crystalline powder, m. p.  $139-141^{\circ}$ .  *$\beta$ -Naphthaleneazo-p-cresol* forms yellow crystals, m. p.  $167^{\circ}$ ; the *acetate*,  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$ , is a yellowish-red, crystalline powder, m. p.  $95-96^{\circ}$ ; the *O-acetylhydrazo*-compound is a white powder.

W. H. G.

**Migration of Acid Residues in the Phenylhydrazones of Acylated *o*-Hydroxyaldehydes.** KARL AUWERS [with K. HANNEMANN] (*Annalen*, 1909, 365, 314-342. Compare preceding abstracts).—The hydrazones described in this paper were prepared by the action of the hydrazine on the aldehyde in alcoholic solution. The *O*-acetyl derivatives were usually obtained by treating the hydrazone in pyridine with acetyl chloride; in some cases they were more readily obtained from the acetyl-aldehyde. The diacetates, prepared by heating the hydrazone with acetic anhydride and sodium acetate, yield on partial hydrolysis with alcoholic alkali hydroxide the corresponding *N*-acetyl derivatives. The benzoates were prepared by condensation of the hydrazine with the aldehyde-benzoate; a few were prepared from the hydrazone by benzoylation in pyridine. Boiling with excess of benzoyl chloride yielded the dibenzoates, which, when warmed with alcoholic alkali, were transformed into the *N*-benzoyl compounds.

The transformation of the *O*-esters into the corresponding *N*-acyl compounds was performed generally by boiling gently with ten times the quantity of glacial acetic acid. The values given in brackets later represent the times required to effect this change completely, unless otherwise stated. In some cases, the conversion of the *O*-acyl compound into the *N*-compound is accompanied by other reactions. For example, *O*-benzoylsalicylaldehyde-*p*-chlorophenylhydrazone is not only converted into the *N*-benzoyl compound, but is also split by the acetic acid into benzoylsalicylaldehyde and *p*-chlorophenylhydrazine; the *N*-benzoyl compound is similarly decomposed. As a result, the various substances interact, and the product of the transformation is a mixture of the *O*-benzoate, *N*-benzoyl compound, dibenzoate, and *p*-chlorophenylhydrazine. The following are the new compounds described.

Salicylaldehydephenylhydrazone-*O*-acetate is converted completely in three hours into the *N*-acetyl compound,  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ , prisms, m. p.  $158-159^{\circ}$ . The *O*-benzoate requires seven hours for its conversion into the *N*-benzoyl derivative,  $\text{C}_{20}\text{H}_{18}\text{O}_2\text{N}_2$ , white, felted needles, m. p.  $169^{\circ}$ .

Salicylaldehyde-*o*-tolylhydrazone,  $\text{C}_{14}\text{H}_{14}\text{ON}_2$ , yellow needles, m. p.  $110-111^{\circ}$ ; *O*-acetate,  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$ , pale yellow needles, m. p.  $111.5^{\circ}$  (three hours); *N*-acetyl derivative, white, rhombic crystals, m. p.  $121-122^{\circ}$ ; *O*-benzoate,  $\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}_2$ , yellow, silky needles, m. p.

157—158° (eight hours); *N*-benzoyl derivative, small, white needles, m. p. 184°.

*Salicylaldehyde-o-amisylhydrazone*,  $C_{14}H_{14}O_2N_2$ , yellow needles, m. p. 93—94°; *O*-acetate,  $C_{16}H_{18}O_3N_2$ , yellow needles, m. p. 112—113° (three hours); *diacetate*,  $C_{18}H_{18}O_4N_2$ , white needles, m. p. 155—156°; *N*-acetyl derivative, small, white needles, m. p. 120°; *O*-benzoate,  $C_{21}H_{18}O_3N_2$ , lemon-yellow needles, m. p. 157—158° (sixteen hours); *N*-benzoyl derivative, slender, white needles, m. p. 158—159°; *di*-benzoate, slender, white needles, m. p. 178°.

*Salicylaldehyde-o-chlorophenylhydrazone*,  $C_{17}H_{11}ON_2Cl$ , compact tetrahedra, m. p. 123°, the *O*-acetate, m. p. 105—106°, passes with great readiness into the *N*-acetyl derivative, m. p. 153—154°; the *O*-benzoate,  $C_{20}H_{15}O_3N_2Cl$ , white needles, m. p. 164°, is recovered unchanged after heating for sixteen hours with acetic acid.

*Salicylaldehyde-m-chlorophenylhydrazone*, stellate groups of light brown needles, m. p. 163—164°; *O*-benzoate, tufts of lemon-yellow, sword-shaped needles, m. p. 142—143°, partly converted in seven hours by boiling acetic acid into the *N*-benzoyl derivative, compact, granular crystals, m. p. 168—170°.

*Salicylaldehyde-p-chlorophenylhydrazone*, pale yellow leaflets, m. p. 169—170°; the *O*-benzoate, long, flexible, silky, yellow needles, m. p. 176—177°, is not converted completely, even after twenty hours, into the *N*-benzoyl derivative, white, felted needles, m. p. 166—167°.

*Salicylaldehyde-p-bromophenylhydrazone* *O*-acetate,  $C_{15}H_{13}O_2N_2Br$ , pale yellow, rhombohedral leaflets, m. p. 119—120° (three hours); *N*-acetyl derivative, tufts of light brown, pointed crystals, m. p. 148—149°; *diacetate*,  $C_{17}H_{15}O_3N_2Br$ , white needles, m. p. 152°; the *O*-benzoate,  $C_{20}H_{15}O_3N_2Br$ , yellow, silky needles, m. p. 186°, is converted into the *N*-benzoyl derivative, white needles, m. p. 163—164°, when boiled with glacial acetic acid, but other reactions take place simultaneously; the *di*-benzoate,  $C_{27}H_{19}O_6N_2Br$ , forms long, white needles, m. p. 156°.

*Salicylaldehyde-o-bromophenylhydrazone*,  $C_{18}H_{11}ON_2Br$ , yellow, pointed crystals, m. p. 111—112°; *O*-acetate, white needles, m. p. 114° (three to four hours); *N*-acetyl derivative, rosettes of pointed crystals, m. p. 142—143°; the *O*-benzoate, pale yellow, glistening leaflets, m. p. 164°, remains unchanged when boiled with acetic acid for twenty hours.

*Salicylaldehyde-o-nitrophenylhydrazone* *O*-acetate,  $C_{15}H_{13}O_4N_3$ , crystallises in soft, flexible, light red needles, m. p. 160°; it does not change into the *N*-acetyl derivative.

*Salicylaldehyde-m-nitrophenylhydrazone* *O*-acetate, red, ellipsoidal needles, m. p. 165° (seven hours); the *N*-acetyl derivative crystallises in lemon-yellow, compact needles, m. p. 164°, and white, felted needles, m. p. 162—163°; the *diacetate*,  $C_{17}H_{15}O_5N_3$ , forms white leaflets, m. p. 149—150°; the *O*-benzoate,  $C_{20}H_{15}O_4N_3$ , long, yellow needles, m. p. 177°, does not change into the *N*-benzoyl derivative.

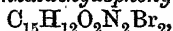
The *O*-acetate of *salicylaldehyde-p*-nitrophenylhydrazone crystallises in red needles, m. p. 185—186°, and with  $\frac{1}{2}C_6H_6$  in yellow needles, m. p. 185—186°; the *O*-benzoate forms soft, yellow, felted needles, m. p. 207—208°; neither of these esters undergoes transformation into

the corresponding *N*-derivative; the *diacetate* forms small, white, felted needles, m. p. 164·5°.

*Salicylaldehyde-o-cyanophenylhydrazone*,  $C_{14}H_{11}ON_3$ , small, yellow needles, m. p. 163°; the *O*-benzoate,  $C_{21}H_{15}O_2N_3$ , light yellow needles, m. p. 164—165°, is decomposed when boiled with glacial acetic acid.

*Salicylaldehyde-m-2-xylylhydrazone O*-benzoate,  $C_{22}H_{20}O_2N_3$ , yellow needles, m. p. 100° (eight hours); *N*-benzoyl derivative, colourless needles, m. p. 179°.

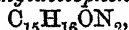
3 : 5-Dibromo-2-hydroxybenzaldehydephenylhydrazone *O*-acetate,



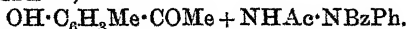
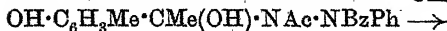
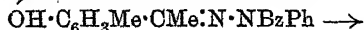
yellow, felted prisms, m. p. 166—167° (fourteen hours); the *N*-acetyl derivative, m. p. 188°, was incorrectly described by Rössing as the *O*-acetate (Abstr., 1885, 388); the *diacetate* has m. p. 164—165°; Rössing gives m. p. 158° (*loc. cit.*); the *O*-benzoate,  $C_{20}H_{14}O_2N_2Br_2$ , forms slender, yellow prisms, m. p. 211—212° (twelve hours); the *N*-benzoyl derivative forms slender, white prisms, m. p. 174°.

*o*-Nitrosalicylaldehydephenylhydrazone *O*-benzoate, light brown needles, m. p. 204—205° (eight hours); *N*-benzoyl derivative, yellow, felted needles, m. p. 199—200°. The *O*-benzoate of the corresponding *p*-nitro-compound forms light red needles, m. p. 230° (eight hours); *N*-benzoyl derivative, white needles, m. p. 260°. W. H. G.

Capacity for Transformation of Acyl Derivatives of the Phenylhydrazones of *o*-Hydroxyketones. KARL AUWERS [with H. DANNEHL] (*Annalen*, 1909, 365, 343—352. Compare preceding abstracts).—2-Hydroxy-5-methylacetophenonephenylhydrazone,

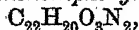


prepared from *o*-acetyl-*p*-cresol and phenylhydrazine, forms compact, glistening, pale yellow plates, m. p. 152·5°; the crystalline *O*-acetate,  $C_{17}H_{18}O_2N_2$ , has m. p. 99°, and is converted when boiled for eight hours with glacial acetic acid into the *N*-acetyl derivative, compact, straw-yellow prisms, m. p. 105°; the *O*-benzoate,  $C_{22}H_{20}O_2N_2$ , forms soft, yellow needles, m. p. 154°, and when boiled with glacial acetic acid for three to four hours, yields *o*-acetyl-*p*-cresol and acetylbenzoylphenylhydrazine, thus:  $OBz \cdot C_6H_3Me \cdot CMe \cdot N \cdot NHPh \rightarrow$



2-Hydroxy-5-methylbenzophenonephenylhydrazone,  $C_{20}H_{18}ON_2$ , crystallises in pale yellow prisms, m. p. 135·5°; the crystalline *O*-acetate,  $C_{22}H_{20}O_2N_2$ , has m. p. 107—108°, and is not converted by boiling glacial acetic acid into the *N*-derivative. Attempts to prepare the latter directly were unsuccessful. The hydroxy-compound is converted by acetic anhydride and sodium acetate into what is probably a *diacetate*, m. p. 107—108°, which is hydrolysed by cold alcoholic alkali, yielding the *N*-acetyl derivative (?), m. p. 147—148°.

2-Hydroxy-5-methoxybenzophenonephenylhydrazone *O*-acetate,



forms compact, yellow prisms, m. p. 134°, and is not changed by hot glacial acetic acid; all attempts to prepare the *N*-derivative were fruitless. W. H. G.

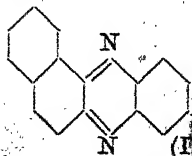
**Reduction Products of  $\beta$ -Naphthaquinonehydrazones [2-Benzeneazo- $\alpha$ -naphthols].** EMILIO NOELTING, EUGÈNE GRANDMOUGIN, and H. FREIMANN (*Ber.*, 1909, 42, 1377—1386).—Noelting and Grandmougin (*Abstr.*, 1891, 1076) arrived at the conclusion that  $\beta$ -naphthaquinonehydrazones must be regarded as 2-azo-derivatives of  $\alpha$ -naphthol, and that the ethers of these hydrazones are true oxygen ethers, since reduction by means of stannous chloride and hydrochloric acid yields, besides ethers of aminonaphthols, aniline, and not an alkylated aniline. These reductions are, however, more complicated than the above results indicate, the ethyl and methyl ethers and the acetyl derivative of 2-benzeneazo- $\alpha$ -naphthols always yielding a considerable proportion of a base,  $C_{16}H_{14}N_2$ , which is probably 2-amino-1-anilinonaphthalene; the latter may be formed from the 2-benzeneazo- $\alpha$ -naphthol derivative by a re-arrangement somewhat similar to the benzidine conversion with simultaneous displacement of the hydroxyl group. The product obtained by Harden (*Abstr.*, 1890, 630) by the action of phenylhydrazine on nitroso- $\beta$ -naphthylamine, and described by him as 2-amino-1-anilino-naphthalene, probably has some other constitution. It is strange that this base is not obtained by reduction of 2-benzeneazo- $\alpha$ -naphthol itself. The reductions of the ethers and of the acetyl derivative give also other compounds, the constitutions of which have not been determined; thus, the acetyl derivative yields a crystalline base, m. p. 124—125°, in small quantity.

2-Amino-1-anilinonaphthalene (?),  $NH_2 \cdot C_{10}H_6 \cdot NHPh$ , separates from benzene or alcohol in granular crystals, m. p. 170°, and with organic solvents gives solutions exhibiting faint blue fluorescence. Its *sulphate*,  $2(C_{16}H_{14}N_2) \cdot H_2SO_4$ , *chloride*,  $C_{16}H_{14}N_2 \cdot HCl$ , *acetyl* derivative,  $C_{18}H_{16}ON_2$ , m. p. 200°, and *benzoyl* derivative, m. p. 239°, were prepared. By the action of nitrous acid, the base is converted into an *azoimide*,  $C_{16}H_{11}N_3$ , which separates from light petroleum in large crystals, m. p. 77°. When distilled with lead oxide, 2-amino-1-anilinonaphthalene yields phenonaphthazine, m. p. 142°, also yielded by the isomeric 1-amino-2-anilinonaphthalene, whilst when boiled with benzil in acetic acid solution it yields the corresponding azonium base, m. p. 215°.

The methyl ether of 2-benzeneazo- $\alpha$ -naphthol has m. p. 102—103°: McPherson (*Abstr.*, 1900, i, 123) gave 95°. On reduction, this ether gives 2-amino-1-anilinonaphthalene, aniline, and 2-amino-1-methoxy-naphthalene,  $NH_2 \cdot C_{10}H_6 \cdot OMe$ , which crystallises in readily volatile, shining leaflets, m. p. 48—49°, forms with organic solvents solutions showing blue fluorescence, and yields an *acetyl* derivative,  $C_{18}H_{13}O_2N$ , m. p. 132°.

The ethyl ether of 2-benzeneazo- $\alpha$ -naphthol, obtained by Meldola and Hanes (*Trans.*, 1894, 65, 834) as a viscid, red oil, forms crystals, m. p. 44°. On reduction, it yields 2-amino-1-anilinonaphthalene, aminonaphthol, aniline, and 2-amino-1-ethoxy-naphthalene,  $NH_2 \cdot C_{10}H_6 \cdot OEt$ , which forms volatile, white leaflets, m. p. 48—49°, and yields an *acetyl* derivative, m. p. 147—148°.

The *acetyl* derivative of  $\beta$ -naphthaquinone-*p*-phenylhydrazone (2-*p*-tolueneazo- $\alpha$ -naphthol), m. p. 102°, gives, on reduction with stannous chloride



and hydrochloric acid, a base, m. p.  $118^{\circ}$ , which, when distilled with lead oxide, yields a new *tolunaphthazine* (formula I), m. p.  $179^{\circ}$ , showing the characteristic azine reactions. T. H. P.

**Acylazoaryl Compounds and Behaviour of Certain Diazo-salts towards Ethers.** GIACOMO PONZIO and G. CHARRIER (*Atti R. Accad. Sci. Torino*, 1909, 44, 295—313).—The oxidation of the hydrazo-group in compounds such as  $\alpha$ -benzoyl- $\beta$ -phenylhydrazine, with formation of the corresponding azo-derivative, can be readily effected by passing nitrous anhydride into ether containing the hydrazo-compound in suspension, the liquid being kept cold and well shaken. The acylazoaryl compounds thus obtained are readily crystallisable, red or brown substances, which are reduced easily, and in the cold, by phenylhydrazine, giving the hydrazo-compounds from which they are prepared:  $R \cdot CO \cdot N : NAr + NHPh \cdot NH_2 = R \cdot CO \cdot NH \cdot NHAr + C_6H_6 + N_2$ .

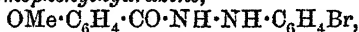
*Benzoylazobenzene*,  $NBz : NPh$ , which crystallises from alcohol in large, red prisms, m. p.  $30^{\circ}$  (decomp.), was obtained by Fischer (*Abstr.*, 1878, 302) as an impure liquid by oxidising  $\alpha$ -benzoyl- $\beta$ -phenylhydrazine in chloroform solution by means of mercuric oxide, and was named by him diazobenzene benzoate.

*Anisoylazobenzene*,  $OMe \cdot C_6H_4 \cdot CO \cdot N_2Ph$ , crystallises from alcohol in amethyst-red plates, m. p.  $40^{\circ}$ , and, in alcoholic solution, is reduced to  $\alpha$ -anisoyl- $\beta$ -phenylhydrazine by means of zinc dust and acetic acid.

*p-Toluylazobenzene*,  $C_6H_4Me \cdot CO \cdot N_2Ph$ , crystallises from alcohol in large, red prisms, m. p.  $41^{\circ}$ .

*Anisoylazo-p-bromobenzene*,  $OMe \cdot C_6H_4 \cdot CO \cdot N_2 \cdot C_6H_4Br$ , crystallises from alcohol in garnet-red, flattened needles, m. p.  $72^{\circ}$ .

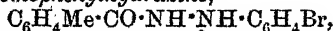
*$\beta$ -Anisoyl- $\alpha$ -p-bromophenylhydrazine*,



obtained as hydrochloride by the interaction of *p*-bromophenylhydrazine (2 mols.) and anisoyl chloride (1 mol.) in ethereal solution, crystallises from alcohol in white laminæ, m. p.  $183^{\circ}$  (decomp.).

*p-Toluylazo-p-bromobenzene*,  $C_6H_4Me \cdot CO \cdot N_2 \cdot C_6H_4Br$ , crystallises from alcohol in brown laminæ, m. p.  $98^{\circ}$ .

*$\beta$ -p-Toluyl- $\alpha$ -p-bromophenylhydrazine*,

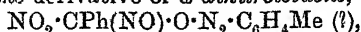


prepared from *p*-bromophenylhydrazine and *p*-toluyl chloride, crystallises from alcohol in shining, white needles, m. p.  $202^{\circ}$  (decomp.).

It has been found previously (*Abstr.*, 1908, i, 482) that the diazobenzene derivative of  $\omega$ -dinitrotoluene, dissolved in moist ether, undergoes intramolecular rearrangement, yielding  $\omega$ -benzeneazo- $\omega$ -dinitrotoluene, and (this vol., i, 338) that, under similar conditions, the *p*-bromodiazobenzene derivative of  $\omega$ -dinitrotoluene is transformed into benzoylazo-*p*-bromobenzene. The authors now describe experiments made with a view to ascertain the influence exerted on this reaction by the nature of the diazo-derivative employed. It is found that, whilst the *o*-diazotoluene, *o*-chlorodiazobenzene, and *o*-bromodiazobenzene derivatives of  $\omega$ -dinitrotoluene are transformed into the isomeric  $\omega$ -*o*-tolueneazo-,  $\omega$ -*o*-chlorobenzeneazo-, and  $\omega$ -*o*-bromobenzeneazo-derivatives of  $\omega$ -dinitrotoluene, the isomeric *p*-compounds are converted into the benzoylazo-derivatives of *p*-toluene, *p*-chloro-

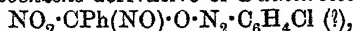
and *p*-bromo-benzene, losing two atoms of nitrogen and three of oxygen in the form of nitrous compounds (compare this vol., i, 338).

The *o*-diazotoluene derivative of *ω*-dinitrotoluene,



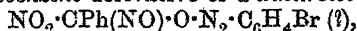
prepared from *o*-diazotoluene acetate and the potassium derivative of *ω*-dinitrotoluene, is obtained as a yellow powder, m. p. 58° (decomp.), dissolves in concentrated sulphuric acid, giving an emerald-green solution, and, when heated with alcohol, is partly oxidised to acet-aldehyde with evolution of nitrogen and partly transformed into *ω*-*o*-tolueneazo-*ω*-dinitrotoluene,  $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , which is also formed in a moist ethereal solution of the preceding compound and separates in shining, red needles, m. p. 137° (decomp.).

The *o*-chlorodiazobenzene derivative of *ω*-dinitrotoluene,



is a yellow powder, m. p. 56° (decomp.), gives an emerald-green solution with concentrated sulphuric acid, and, when heated with alcohol, is partly oxidised with evolution of nitrogen and partly transformed into *ω*-*o*-chlorobenzeneazo-*ω*-dinitrotoluene,  $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Cl}$ , which is deposited in shining, orange-red laminae, m. p. 140° (decomp.).

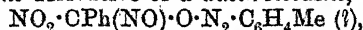
The *o*-bromodiazobenzene derivative of *ω*-dinitrotoluene,



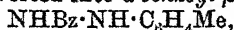
is a yellow powder m. p. 65° (decomp.).

*ω*-*o*-Bromobenzeneazo-*ω*-dinitrotoluene,  $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Br}$ , separates in orange-coloured laminae, m. p. 140° (decomp.).

The *p*-diazotoluene derivative of *ω*-dinitrotoluene,



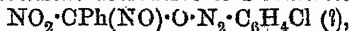
is a yellow powder, m. p. 74° (decomp.). When dissolved in moist ether, it is converted into *benzoylazo-p*-toluene, which could not be crystallised, and, on reduction with zinc and acetic acid in alcoholic solution, is converted into *α*-benzoyl-*β*-*p*-tolylhydrazine,



crystallising from benzene in shining, white laminae, m. p. 145—146°, and obtainable also by the interaction of *p*-tolylhydrazine (2 mols.) and benzoyl chloride (1 mol.) in ethereal solution.

*ω*-*p*-Tolueneazo-*ω*-dinitrotoluene,  $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , prepared by heating the *p*-diazotoluene derivative of *ω*-dinitrotoluene with alcohol, crystallises from chloroform in orange-red laminae, m. p. 153—154° (decomp.).

The *p*-chlorodiazobenzene derivative of *ω*-dinitrotoluene,



is a yellow powder, m. p. 61° (decomp.), and, when dissolved in moist ether, is converted into *benzoylazo-p*-chlorobenzene,  $\text{NBz} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Cl}$ , which crystallises from light petroleum in orange-yellow laminae, m. p. 73°.

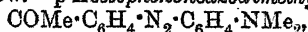
*α*-Benzoyl-*β*-*p*-chlorophenylhydrazine,  $\text{NHBz} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$ , prepared by reducing the preceding compound or by the interaction of *p*-chlorophenylhydrazine (2 mols.) and benzoyl chloride (1 mol.), crystallises from benzene in white laminae, m. p. 153°. When suspended in anhydrous ether and oxidised by means of nitrous anhydride, it is transformed into *benzoylazo-p*-chlorobenzene.

*ω*-*p*-Chlorobenzeneazo-*ω*-dinitrotoluene,  $\text{CPh}(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{Cl}$ , crystal-

lises from chloroform in shining, orange-yellow needles, m. p. 161° (decomp.).  
T. H. P.

**Some Azo-dyes from *p*-Aminoacetophenone.** HENRY A. TORREY and WARREN MACPHERSON (*J. Amer. Chem. Soc.*, 1909, 31, 579—583).—As very few azo-dyes derived from *p*-aminoacetophenone have hitherto been described, some of these compounds have now been prepared. The aminoazo-compounds obtained have been found to change from yellow to red on the addition of acids. Determinations of the sensitiveness of *p*-acetophenoneazo-diphenylamine, -dimethylaniline, and -diethylaniline, and the oxime of the last, by a method similar to that of Salm's (*Abstr.*, 1906, ii, 218) showed that the hydrogen ion concentration at which the change in colour occurs is about  $5 \times 10^{-5}$  in the case of *p*-acetophenoneazo-diethylaniline, whilst the other compounds are less sensitive, *p*-acetophenoneazodiphenylamine being the least so. In preparing *p*-acetophenoneazodiphenylamine, the diazotised solution was added to a solution of diphenylamine in a large quantity of glacial acetic acid. This method is recommended for the preparation of phenylaminoazobenzene and other azo-compounds of weak bases which are not readily soluble in dilute mineral acids.

*p*-Acetophenoneazoresorcinol,  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , m. p. 215—220° (decomp.), crystallises in deep orange-red needles, and dissolves in dilute alkali hydroxide to form a deep red solution which dyes silk bright yellow. *p*-Acetophenoneazodimethylaniline,



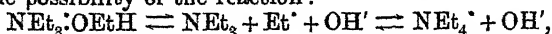
m. p. 203—204°, forms red crystals, and yields a purple hydrochloride; its oxime, m. p. 242—243°, forms orange-red crystals. *p*-Acetophenoneazodiethylaniline,  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NEt}_2$ , m. p. 162—163°, dissolves in dilute acids to form a crimson solution, which dyes silk deep orange-red; the oxime melts at 199—200°. *p*-Acetophenoneazodiphenylamine,  $\text{COMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{NHPh}$ , m. p. 184—185°, crystallises in long, red prisms and gives a bright purple solution with acids, which dyes silk and wool a poor shade of orange-yellow. *p*-Acetophenoneazo- $\beta$ -naphthol, m. p. 181—183°, forms small, red prisms, and is insoluble in aqueous alkali (compare Klingel, *Abstr.*, 1886, 61); its oxime was prepared.  
E. G.

***p*-Nitrobenzenediazonium Chloride.** CARL G. SCHWALBE (*Ber.*, 1909, 42, 1425. Compare *Abstr.*, 1905, i, 952).—A criticism of the statements and conclusions of Bucherer and Wolff (*this vol.*, i, 272) as to the stability and use of "nitrosoamine paste" for preparing a nitrous acid-free solution of *p*-nitrodiazobenzene.

J. V. E.

**Constitution of Diazonium and Ammonium Salts.** JOHN C. CAIN (*Ber.*, 1909, 42, 1208—1211. Compare *this vol.*, i, 70).—Polemical. It is pointed out in reply to Hantzsch (*this vol.*, i, 193) that: (1) benzenediazonium chloride and *p*-benzoquinone chloroimide are exceedingly similar in their properties; (2) diazo-salts and

quinones behave similarly towards bromine. It is possible that the diazo-perbromides are analogous in constitution to benzoquinone dibromide; (3) the reduction of azobenzene to hydrazobenzene is not accompanied by separation of the nitrogen atoms, and, therefore, a substance having the formula given by the author to benzenediazonium chloride need not necessarily yield a diamine when reduced. (4) The Blomstrand formulation does not account for the formation of a diazo-salt from *ar*-naphthylamine and the non-formation of a diazo-compound from *ac*-naphthylamine. The reason of this different behaviour, according to the author's theory, is due to the fact that only in the former case is the formation of a quinonoid system possible. (5) Although ethyl alcohol and triethylamine do not combine under ordinary conditions, this is no argument against the possibility of the reaction:



since ethyl alcohol, under ordinary conditions, does not exist in the dissociated state. W. H. G.

**Hydrolysis of Crystallised Albumin from the Hen's Egg.** THOMAS B. OSBORNE, D. BREESE JONES, and CHARLES S. LEAVENWORTH (*Amer. J. Physiol.*, 1909, 24, 252—262).—Estimations of the products of acid hydrolysis were made, the total yield accounting for 50% of the protein. Glucosamine was present to the extent of 1.23%. The other figures are not widely different from those given by Abderhalden and Pregl, but estimations of diamino-acids are given which were omitted in the work of these observers. The figures obtained by Hugounenq and Morel, who used baryta as the hydrolysing agent, are widely different in most cases from those recorded in the present paper.

W. D. H.

**Partial Hydrolysis of Edestin.** ZDENKO H. SKRAUP and A. WÖBER (*Monatsh.*, 1909, 30, 289—309).—Proteins, such as egg-albumin, casein, edestin, and serum globulin, dissolve in a mixture of equal volumes of fuming hydrochloric and acetic acids. When such solutions are diluted and nearly neutralised with ammonia, amorphous precipitates are obtained, which diminish in amount the more the action of the concentrated acids is prolonged.

One hundred parts of edestin yield thirteen parts of insoluble compound *A*, and twenty-seven parts of the soluble albumose peptone mixture *B*. These substances give different colour reactions from the original edestin. When edestin is converted into substance *A*, not only the proportion of glutamic acid, but also that of tyrosine, phenylalanine, leucine, alanine, glycine, and even arginine diminishes, whereas in the partial hydrolysis of albumin (compare Skraup and Hummelberger, this vol., i, 711) the reverse is the case. In substance *B* as compared with *A* the amount of histidine is distinctly, and that of arginine and glutamic acid largely, increased.

When treated with sodium hydroxide, edestin yields fractions differing in solubility, designated as protalbic and lysalbic acids and lysalbin-peptone. The former gives the same colour reactions as

substance *A*, the later two behave similarly to *B*. In the case of edestin apparently the carbohydrate group remains in the sparingly soluble fraction, whereas in albumin it is found in the most soluble fraction.

E. F. A.

**Hydrolysis of Casein with Hydrochloric and with Sulphuric Acid.** ZDENKO H. SKRAUP and W. TÜRK (*Monatsh.*, 1909, 30, 287—288).—Air-dry casein, hydrolysed either by boiling with fuming hydrochloric acid or with 33% sulphuric acid, yielded 22.3% and 20.3% of crude glutamic acid hydrochloride respectively. This is partly racemised;  $[\alpha]_D + 21.7^\circ$ . Kutscher's statement that much less glutamic acid is obtained on hydrolysis with sulphuric acid is therefore to be corrected.

E. F. A.

**Depression of Freezing Point Due to Caseinates in Solution.** T. BRAILSFORD ROBERTSON and THEO. C. BARNETT (*J. Biol. Chem.*, 1909, 6, 105—114).—Neutral (to litmus) and basic (neutral to phenolphthalein) caseinates of potassium, lithium, ammonium, and calcium, when dissolved in water, depress the freezing point to a definite measurable degree. The results indicate that casein behaves towards bases as a monobasic acid, possessing, when combined with bases in solutions neutral to phenolphthalein, a molecular weight of about 1400, and when combined with bases in solutions neutral to litmus, a molecular weight of about 2000.

W. D. H.

**Nucleo-protein from the Gastric Mucosa.** ARCHIBALD E. OLPP (*Proc. Amer. Soc. Biol. Chem.*, 1908, 1; *J. Biol. Chem.*, 6).—Dilute alkali extracts from the mucous membrane of the stomach a nucleo-protein which is precipitable by acids. The product obtained is free from mucin. A relationship between it and pepsinogen is suggested.

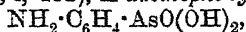
W. D. H.

**Nucleic Acids.** W. A. JACOBS and PHCEBUS A. LEVENE (*Proc. Amer. Soc. Biol. Chem.*, 1908, xxxvi—xxxvii; *J. Biol. Chem.*, 6).—On acid hydrolysis of inosic acid, the levorotatory solution became dextro-rotatory, and from this a reducing crystalline barium salt of a pentose-phosphoric acid was isolated. On alkaline hydrolysis, phosphoric acid was split off without the appearance of free hypoxanthine or sugar in the solution; from this solution a silver compound of a pentose-hypoxanthine complex was obtained; this is not reducing. It is thus proved that the phosphoric acid is bound to one of the hydroxyls of the pentose, and hypoxanthine is linked to the aldehyde group in a glucoside arrangement.

It is considered probable that nucleic acids are built up of "nucleotides," groups similar in composition to that of inosic acid, which are joined together as the phosphoric acid radicles in polyphosphoric acids. From yeast-nucleic acid a substance was isolated as a tetranucleotide, in which the sugar is pentose, and the bases adenine, guanine, uracil, and cytosine.

W. D. H.

Preparation of *m*-Aminophenylarsinic Acid (*m*-Arsanilic Acid). FARBERWERKE FORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 206344).—From the nitrophenylarsinic acid formerly obtained by Michaelis (Abstr., 1902, i, 411), *m*-aminophenylarsinic acid,



colourless prisms, m. p.  $212-214^\circ$ , is obtained by reduction, either with sodium amalgam or ammonium sulphide. In the former case the reduction is effected in methyl-alcoholic solution, and the product precipitated as its zinc salt. In the latter, the aqueous solution of ammonium sulphide is evaporated to dryness, the residue extracted with dilute hydrochloric acid to remove the intermediate products,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsS}_2$  and  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsS}$ , which, after desulphurisation with copper sulphate in alkaline solution, yields an alkali salt of *m*-aminophenylarsinic acid. F. M. G. M.

Preparation of an  $\alpha$ -Naphtholarsinic Acid [4-Hydroxy-naphthalenearsinic Acid]. WILHELM ADLER (D.R.-P. 205775).—4-Aminonaphthalenearsinic acid (prisms, m. p.  $173-175^\circ$ ) is prepared by heating  $\alpha$ -naphthylamine (4 parts) and arsenic acid (3 parts) at  $190^\circ$  until quantitative tests show that the condensation has reached its maximum. The product is extracted with cold aqueous alkali hydroxide and reprecipitated with mineral acids, diazotised in cold 15% hydrochloric acid, and the solution heated to boiling.

The sodium salt of 4-hydroxynaphthalenearsinic acid, colourless needles or leaflets, is precipitated by means of alcohol. The free acid, which is sparingly soluble in water and dissolves readily in alcohol, has an intense action on the skin, and may accordingly be employed in dermatology. F. M. G. M.

Formation of Peroxides in the Oxidation of Organo-magnesium Compounds. HENRI WUYTS (*Compt. rend.*, 1909, 148, 930—931).—The action of oxygen on an ethereal solution of magnesium phenyl bromide leads, not only to the formation of phenol (Bodroux, Abstr., 1903, i, 249), but also to the formation of other phenolic compounds with diphenyl, *p*-diphenylbenzene, phenylethylcarbinol, and ethyl alcohol. The formation of alcohols is explained by the equation:  $\text{PhMgBr} + \text{OEt}_2 + \text{O} = \text{CHMePh} \cdot \text{OH} + \text{OEt} \cdot \text{MgBr}$ .

Probably, however, a peroxide is first formed, since it has been found that a toluene solution of magnesium phenyl bromide, which has been exposed to the action of dry oxygen at a low temperature, is capable of liberating iodine from potassium iodide solutions. Further experiments are described which confirm this supposition.

W. O. W.

## Organic Chemistry.

Catalytic Reactions at High Temperatures and Pressures. XVII. Reduction of Fatty Compounds with an Ethylene Linking in Presence of Cupric Oxide. WLADIMIR IPATIEFF (*Ber.*, 1909, 42, 2089—2092. Compare Sabatier and Senderens, *Abstr.*, 1905, i, 333).—Ethylene is reduced to ethane by hydrogen at 180° under 60 atmospheres' pressure, cupric oxide being used as the catalyst. With nickel oxide, a part of the ethane is always broken down to methane.

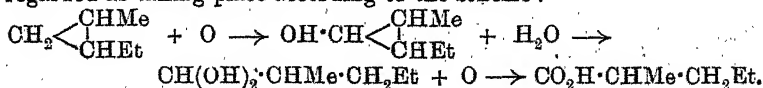
$\beta$ -Methyl- $\Delta^2$ -butylene,  $\text{CMe}_2\text{CHMe}$ , is reduced at 300° under 100 atmospheres to isopentane, a little *tert.*-amyl alcohol being also formed. The reduction at the ordinary pressure in presence of nickel does not take place in such cases, it being necessary that the double linking should be attached to a methylene group.

Under similar conditions, oleic acid yields stearic acid. *cyclo*-Hexene remains unaltered. C. H. D.

Researches in the Hexene and Heptene Series. E. S. PRSCHEVALSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 464—469).—According to Welt (*Abstr.*, 1897, i, 452), *n*-heptylene may be obtained by Kraft's method; namely, by heating corresponding esters of high molecular weight. The author finds, however, that by heating heptyl palmitate, the hydrocarbon obtained is not a definite individual, since on oxidation it yields an acid, the silver salt of which contains more silver than corresponds with silver hexoate. The removal of hydrogen iodide from  $\alpha$ -iodo- $\beta$ -methyl-*n*-pentane results in the formation of a closed-ring compound (compare Zelinsky and Prschevalsky, *Abstr.*, 1908, i, 845).

Reduction of methyl *n*-propyl ketone and treatment of the alcohol thus obtained with hydrochloric acid in a sealed tube at 110—120° yields the chloride,  $\text{CHMePr}^{\alpha}\text{Cl}$ , b. p. 96—97°/746 mm.,  $D_4^{20}$  0.8753,  $D_4^{20}$  0.8704,  $n_D^{19}$  1.4062; for this compound, Wagner and Saytzeff (*Abstr.*, 1876, i, 547) gave the constants: b. p. 103—105°,  $D_4^{20}$  0.912,  $D_4^{21}$  0.891. Treatment of this chloride with magnesium and then with trioxymethylene gives  $\beta$ -methyl-*n*-pentyl alcohol, which, by means of iodine and phosphorus, is converted into  $\alpha$ -iodo- $\beta$ -methyl-*n*-pentane,  $\text{CHMePr}^{\alpha}\text{CH}_2\text{I}$ , b. p. 72—73°/32 mm.,  $D_4^{15}$  1.4496,  $D_4^{20}$  1.4430,  $n_D^{19}$  1.4938. The action of alcoholic potassium hydroxide on this iodide yields 1-methyl-2-ethylcyclopropane,  $\text{CH}_2\text{C} \begin{smallmatrix} \text{CHMe} \\ \text{CHEt} \end{smallmatrix}$ , b. p.

61.5—62.5°/736 mm.,  $D_4^{15}$  0.6867,  $D_4^{20}$  0.6820,  $n_D^{20}$  1.3928. Oxidation of this hydrocarbon by permanganate yields formic, acetic, propionic, butyric, and isohexoic acids. The formation of the last-named acid is regarded as taking place according to the scheme:

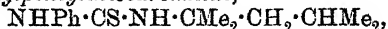


T. H. P.

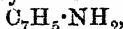
$\beta\delta$ -Dimethylpentane and its Occurrence in Caucasian Naphtha. G. W. CHONIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 327—344).—Part of this paper has been already published (Abstr., 1905, i, 729; *J. Russ. Phys. Chem. Soc.*, 1908, 40, 731; compare also Konowaloff, Abstr., 1906, i, 129).

Nitration of  $\beta\delta$ -dimethylpentane yields mainly the tertiary nitro-derivative,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{NO}_2$ , which on reduction gives the corresponding amine,  $\text{C}_7\text{H}_{15}\cdot\text{NH}_2$ , b. p. 121—122.2°/753 mm. (compare Konowaloff, Abstr., 1908, i, 241); the hydrochloride of the latter,  $\text{C}_7\text{H}_{15}\cdot\text{NH}_2\cdot\text{HCl}$ , m. p. 208—209° (decomp.), and the platinichloride,  $(\text{C}_7\text{H}_{15}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6$ , decomposing at 183°, were prepared.

Phenyl- $\beta\delta$ -diethylpentylthiocarbamide,



prepared by the action of phenylthiocarbimide on the amine,



crystallises from methyl alcohol in colourless, rhombic plates, m. p. 111—112°.

The occurrence of  $\beta\delta$ -dimethylpentane in Caucasian naphtha is demonstrated by the preparation from the latter of the above tertiary nitro-derivative, the corresponding amine, and phenyl- $\beta\delta$ -dimethylpentylthiocarbamide.

T. H. P.

Dipropargyl, its Magnesium Derivative, and  $\Delta^{\beta\epsilon}$ -Hexadiene- $\alpha\zeta$ -dicarboxylic Acid. ROBERT LESPIEAU and VAYON (*Compt. rend.*, 1909, 148, 1331—1333).—When treated with iodine, the copper derivative of dipropargyl yields  $\alpha\alpha\beta\beta\zeta\zeta$ -hexa-iodo- $\Delta^{\beta\epsilon}$ -hexadiene,  $\text{Cl}_2\cdot\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Cl}\cdot\text{Cl}_2$ , m. p. 155—156°. When the magnesium derivative of this substance is treated with carbon dioxide it forms  $\Delta^{\beta\epsilon}$ -hexadiene- $\alpha\zeta$ -dicarboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:\text{C}\cdot\text{CO}_2\text{H}$ , m. p. 190° (decomp.). This acid undergoes reduction to suberic acid when treated in alcoholic solution with hydrogen in the presence of platinum-black.

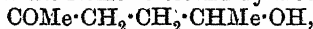
W. O. W.

The Action of Alcohol, its Impurities, and its Denaturing Agents on the Ordinary Metals. RENÉ P. DUCHEMIN (*Bull. Assoc. Chim. suc. dist.*, 1909, 26, 1076—1078).—The metals iron, tin, zinc, copper, and brass were exposed for three months at 18° to the action of pure ethyl and methyl alcohols (95°), and to mixtures of these with 50% of water, with 10% of acetaldehyde, 10% of ethyl acetate, and 10% of amyl acetate respectively in the case of ethyl alcohol, and with 10% of acetone and 10% of methyl acetate in the case of methyl alcohol. The liquids were evaporated, and a table of the weights of the solid remaining is given. Examination of this table shows that addition of acetaldehyde, amyl acetate, and water augments the attack on all the metals, particularly iron and zinc in the latter case, whilst the presence of ethyl acetate increases the action on iron, tin, and zinc, but not on copper or brass. Addition of water to methyl alcohol accelerates the attack on iron, tin, and zinc, but not on copper, and of acetone that on tin and copper, and of methyl acetate on iron, tin and zinc. These results are in accordance with Lindet's results (*ibid.*, 1904—1905, 370).

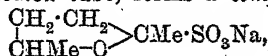
The conclusions are drawn that ethyl and methyl alcohols have a comparable action on metals, and that it is the presence of impurities which causes serious disadvantages in the use of denatured alcohol.

E. H.

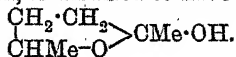
**Hexan- $\epsilon$ -one- $\beta$ -ol.** ANDREAS LIPP and E. SCHELLER (*Ber.*, 1909, 42, 1960—1967).—The interaction of propylene bromide and ethyl sodioacetoacetate (Perkin and Stenhouse, *Trans.*, 1892, 61, 67) has been re-examined. A brominated intermediate compound, analogous to that formed in the case of trimethylene bromide (*Abstr.*, 1886, 218), cannot be detected, and the ethyl 2-acetyl-1-methylcyclopropane-2-carboxylate and ethyl dimethyldehydropentane-carboxylate, which are formed in approximately equal quantities, yield by heating with dilute hydrochloric acid, not acetoisobutyl alcohol as Perkin and Stenhouse assume, but the isomeric secondary alcohol,



the constitution of which is proved by its oxidation to acetonyl-acetone by sodium dichromate and sulphuric acid. The alcohol has b. p. 201—205°/270 mm., reduces warm ammoniacal silver nitrate and Fehling's solutions, yields an *anhydride*, b. p. 70°, when heated at 230° in a sealed tube, forms a *compound*,



with sodium hydrogen sulphite, an oily *oxime*, a *semicarbazone*, m. p. 149—150°, and *esters* of benzoic and acetic acids. Since the esters do not react with hydroxylamine or sodium hydrogen sulphite, the ketol, in alkaline solution, is assumed to have the constitution:



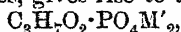
C. S.

**Oxidation of Polyhydric Alcohols by a Peroxydase System.** E. DE STOECKLIN and E. VULQUIN (*Compt. rend.*, 1909, 148, 1404—1406. Compare this vol., i, 196, 198).—It has been shown previously that polyhydric alcohols are not attacked in presence of the system hydrogen peroxide—tannin—iron; when quinol, however, is substituted for tannin, somewhat profound oxidation takes place. The action of this peroxydase system has been studied in connexion with the following alcohols, and in each case the product shows the presence of a ketone or aldehyde. Ethylene glycol is converted into glycollaldehyde. Glycerol forms glyceraldehyde and dihydroxyacetone. Mannitol forms mannose together with a ketone, of which the *osazone* has m. p. 188°. The products of oxidation of dulcitol contain an aldehydic sugar and yield dulcitosazone. In the case of sorbitol, sorbosazone has been isolated from the product together with an unknown osazone crystallising in lamellæ.

W. O. W.

**Preparation of Glycerylphosphates, Particularly Crystallisable Sodium Glycerylphosphates.** LES ÉTABLISSEMENTS POULENC FRÈRES (D.R.-P. 208700).—On heating glycerol in a vacuum with

the metallic or ammonium phosphates of the general formula  $M'H_2PO_4$ , the diglyceryl ester,  $(C_2H_5O_2)_2PO_4M'$ , is produced, and this, on treatment with alkali hydroxides, gives rise to the glyceryl ester,



of which the sodium salt is crystallisable.

F. M. G. M.

### Preparation of Sulphonic Acids of the Aliphatic Series.

ALEXANDER E. ARBUSOFF and P. S. PISHTSCHIMUKI (*J. Russ. Phys.-Chem. Soc.*, 1909, 41, 451—454).—The authors find that for the preparation of Strecker's compounds, from which the corresponding sulphonic acids may be readily obtained, it is unnecessary to heat the mixture of alkyl halide and potassium or sodium sulphite in sealed tubes at  $140^\circ$ , as the reaction takes place at the ordinary temperature. It is found, too, that hydrolysis of ethyl sulphite and its homologues by alkali hydroxides yields the alkali sulphites.

The following Strecker's salts were prepared: (1)  $4Et \cdot SO_3K, KI$ , by hydrolysing ethyl sulphite by means of potassium hydroxide in presence of ethyl iodide; (2)  $4Me \cdot SO_3K, KI$ , from ethyl sulphite, potassium hydroxide, and methyl iodide; and (3)  $4C_2H_5 \cdot SO_3K, KI$ , from ethyl sulphite, potassium hydroxide, and allyl iodide. In all these cases, after removal of the sulphonate from the solution, the latter contained no sulphite, so that the reaction between the alkyl iodide and the sulphite is complete.

T. H. P.

**Constitution of Certain Mercuric Compounds with Complex Cations. III.** VINCENZO BORELLI (*Gazzetta*, 1909, 39, i, 455—477. Compare Abstr., 1908, ii, 1039).—In this paper the author discusses previous work on complex salts formed by mercuric sulphide, and describes *sulphidomercury acetate*,  $Hg_2S(OAc)_2$ , and *sulphidomercury basic acetate*,  $(Hg_2S \cdot Hg_2O)(OAc)_4$ .

Dissolution of mercuric sulphide in mercuric acetate solution causes depressions of the freezing point in amount more than double the theoretical elevations, so that considerable diminution in the concentration of the molecular complexes occurs. Conductivity measurements of these solutions indicate an increase of the specific conductivity, and hence an increase in the number of ions. An explanation is given of these two apparently contradictory observations. Electrolysis of the solutions shows that the mercuric sulphide exists in the form of complex ions, which move towards the cathode under the influence of the current.

General conclusions are drawn from these results and those given in the two preceding papers (Abstr., 1908, i, 515; 1908, ii, 1039).

T. H. P.

**Action of Finely Divided Metals on Aliphatic Acids.** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1909, [iv], 5, 616—623).—Zinc dust decomposes acetic acid, producing hydrogen, carbon dioxide, acetone, and some acetaldehyde. This type of action also takes place with finely divided cadmium, iron, aluminium, lead, and copper, but the temperature at which the reaction commences varies with each metal, as does also the vigour of the action and the relative extent to

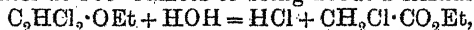
which the various products are formed. With nickel, the chief product of the action is the corresponding lower saturated hydrocarbon, no ketone being produced. When acetic acid vapour is passed over heated zinc dust, it begins to be decomposed at  $250^{\circ}$ , yielding hydrogen and zinc acetate, and if the action is continued at  $250-280^{\circ}$ , hydrogen is replaced by carbon dioxide, and acetone accompanied by some acetaldehyde distills over. After a time all action ceases, and the acid is no longer decomposed. If the temperature is now raised to  $420^{\circ}$ , the zinc oxide remaining in the tube begins to form acetone and carbon dioxide from the acetic acid vapour catalytically (compare Senderens, Abstr., 1908, i, 494). Under the same conditions and at a temperature of  $280-290^{\circ}$ , propionic, butyric, isobutyric, isovaleric, hexoic, octoic, and nonoic acids are decomposed by zinc dust, yielding, like acetic acid, the corresponding aldehyde and symmetrical ketone. Finely divided cadmium reacts with acetic acid vapour in much the same way as zinc dust. At  $315^{\circ}$  the gas evolved is about 92% carbon dioxide and 8% hydrogen, and the ratio of acetaldehyde to acetone in the distillate is 1:7. The residue in the tube at the end of the experiments consists mainly of unchanged metal with a little cadmium oxide. The higher homologues of acetic acid already mentioned are also decomposed by finely divided cadmium, the symmetrical ketone in each case being the chief product of the reaction.

With finely divided nickel at  $230^{\circ}$ , propionic acid yields a little acetaldehyde, but ethane and carbon dioxide are the chief products, and, similarly, butyric and isobutyric acids yield each a little of the corresponding aldehyde, but the chief product in each case is propane.

With finely divided copper, reaction sets in at  $380-400^{\circ}$ , and a little of the symmetrical ketone, corresponding with the acid, is formed, accompanied by saturated hydrocarbons. With iron the action commences at  $240^{\circ}$ , and the sole products are the corresponding ketone and carbon dioxide. With aluminium, action takes place normally at  $380^{\circ}$ , a little aldehyde being formed in addition to the ketone, and with lead, action begins at  $300^{\circ}$ , becomes rapid at  $350^{\circ}$ , and is quite normal.

T. A. H.

**Production of Alkyl Chloroacetates from Dihalogenated Vinyl Ethers.** GEORGES IMBERT UND CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE (D.R.-P. 209268).—Dihalogenated vinyl ethers and alcohol interact, forming ethyl chloride and alkyl monohalogenated acetate,  $C_2HCl_2 \cdot OEt + EtOH = EtCl + CH_2Cl \cdot CO_2Et$ . It has now been found that water at  $100^{\circ}$  suffices to bring about a similar change:



and in this way ethyl chloroacetate is produced from ethyl dichloro-vinyl ether.

F. M. G. M.

**True Nitroso-derivatives of the Esters of Aliphatic Carboxylic Acids.** JULIUS SCHMIDT and KARL TH. WIDMANN (*Ber.*, 1909, 42, 1886—1902. Compare this vol., i, 134).—By the action of the nitrous gases from arsenious oxide and nitric acid, it has been found possible to replace an acetyl by a nitroso-group in the following compounds provided a solvent is not used: Ethyl diacetylsuccinate, and the

ethyl esters of methyl-, ethyl-, and butyl-acetoacetic acids. The compounds thus formed are the esters of nitroso-derivatives of aliphatic acids, e.g.,  $\text{Ac}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} \rightarrow \text{O}\cdot\text{N}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ .

The compounds obtained are blue or bluish-green liquids with a penetrating odour. The depth of colour and also the stability of the compound increases with the complexity of the alkyl group present. When kept for some time at the ordinary temperature, or more quickly when shaken with water or alkalis, the blue colour disappears. This is partly due to conversion into the corresponding colourless oximino-derivatives and partly to polymerisation. They all give the Liebermann nitroso-reaction, and decompose when distilled under reduced pressure. When reduced, they yield esters of amino-acids, and when oxidised, esters of nitro-aliphatic acids. The latter are pale yellow oils which cannot be distilled under reduced pressure; when strongly heated they explode.

The following compounds have been prepared: *ethyl a-nitroso-propionate*,  $\text{NO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ ; *ethyl a-nitroso-n-butyrate*,  $\text{NO}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ ;

*ethyl a-nitrosohexoate*,  $\text{NO}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}_2\text{Et}$ ,  $D_{18}^{18}$  1.24,  $n_D^{18}$  1.6251; the corresponding nitro- and amino-derivatives; *ethyl a-nitroso-β-acetylsuccinate*,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{NO})\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ . J. J. S.

**Petroselic Acid. A New Acid of the Oleic Acid Series.** EDUARD VONGERICHTEN and A. KÖHLER (*Ber.*, 1909, 42, 1638—1639).—The *fat*,  $\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ , isolated from oil of parsley seeds has m. p. 32°, solidifies at 16.5°, has  $n_D^{40}$  1.4619, saponification number 191.2, iodine number 84.3, and is hydrolysed by alcoholic potassium hydroxide, yielding *petroselic acid*,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ , m. p. 33—34°, solidifying at 27°,  $D_{40}^{40}$  0.8681,  $n_D^{40}$  1.4533, of which the *amide*,  $\text{C}_{17}\text{H}_{33}\cdot\text{CO}\cdot\text{NH}_2$ , has m. p. 76°, and the *lead*, *barium*, *zinc*, *magnesium*, and *silver* salts are mentioned. The new acid has iodine number 89.9, Köttsstorfer's index 198.6, acetyl number 0, yields with a trace of nitrous acid an *acid*,  $\text{C}_{18}\text{H}_{34}\text{O}_3$ , m. p. 54°, analogous to elaidic acid, and combines with bromine to form a *dibromide*, which, with methyl-alcoholic potassium hydroxide under pressure, yields an *analogue* of stearolic acid,  $\text{C}_{18}\text{H}_{32}\text{O}_2$ , m. p. 54°, which is converted by Baruch's method into a *ketonic acid*,  $\text{C}_{18}\text{H}_{34}\text{O}_3$ , m. p. 80°, the oxime of which by fission, after undergoing the Beckmann transformation, yields lauric and pimelic acids and undecylamine. Petroselic acid is oxidised by alkaline potassium permanganate to a *dihydroxystearic acid*, m. p. 122°, and forms an ozonide which yields lauric acid by decomposition. The results indicate that petroselic acid has the constitution  $\text{CH}_3\cdot[\text{CH}_2]_{10}\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$ . C. S.

**Crotonic Anhydride.** ANDREAS LUNIAK (*Ber.*, 1909, 42, 1854).—The crotonic anhydride described by the author as new (this vol., i, 284) has been previously prepared by Clover and Richmond (*Abstr.*, 1903, i, 397). C. H. D.

**Gluconic Acid from an Efflorescence on the Walls of a Sugar Cane.** VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1909, 33, 547—551).—The efflorescence which had formed during

several years was a brown substance, in some places mixed with moulds. It contained: water, 13.60; insoluble organic matter, 5.15; sand, 3.25;  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , 0.25;  $\text{CaO}$ , 8.35;  $\text{MgO}$ , 0.22; alkalis, 2.50, and soluble organic matter, 66.68%. One kilo. of the substance when extracted with water yielded 450 grams of basic calcium gluconate, from which the lactone (m. p.  $132^\circ$ ) was obtained and analysed. The substance was further identified by means of the zinc salt and the phenylhydrazide.

The production of gluconic acid is attributed to the action of micro-organisms, *Micrococcus oblongus* (Boutroux, *Compt. rend.*, 1880, 91, 236) or *Bacterium xylinum* (Beyerinck, *ibid.*, 1884, 98, 995), on glucose.

N. H. J. M.

**Preparation of Ketonesulphoxylates.** FARBWERKE VORM. MEISTER, LUCAS & BRÜNING (D.R.-P. 207846).—Sodium acetone-sulphoxylate,  $\text{O}_2\text{H}_5\text{O}\cdot\text{NaHSO}_2\cdot\text{H}_2\text{O}$ , colourless needles, easily soluble in water and also in alcohol, is obtained by adding zinc dust to an aqueous solution of acetone and sodium hydrogen sulphite. The reduction may also be effected by powdered iron and acetic acid.

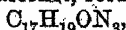
Sodium methyl-ethyl-ketone-sulphoxylate is similarly prepared from methyl ethyl ketone, the yield being 80–90%. These ketone-sulphoxylates are less stable than the formaldehydesulphoxylates, and reduce indigotin and naphthylamine Bordeaux even in the cold.

F. M. G. M.

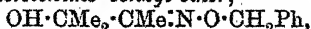
**Action of Alkali Dichromates on Agaricic Acid.** J. D. RIEDEL (*Chem. Zentr.*, 1909, i, 1403; from *Gesch. Ber.*, 1909, 9–10).—Methyl heptadecyl ketone,  $\text{C}_{17}\text{H}_{35}\cdot\text{CO}\cdot\text{CH}_3$  (Abstr., 1908, i, 4), has been prepared in a high state of purity and in good yield (60–70%) from agaricic acid by dissolving it in glacial acetic acid and warming with an alkali dichromate. Thus prepared, it forms colourless crystals, m. p.  $55.5^\circ$ , and gives an oxime, m. p.  $76.5$ – $77.5^\circ$ .

J. V. E.

**Ethers of Oximinoketones.** OTTO DIELS and FRITZ TER MEER (*Ber.*, 1909, 42, 1940–1945).—The behaviour of oximinoketones and their ethers towards Grignard reagents recalls that towards aldehydes and ketones (Abstr., 1905, i, 509; 1907, i, 466); the ethers alone react. The interaction of magnesium methyl iodide and diacetylmonoxime methyl ether in cold ethereal solution leads to the formation of trimethylketoloxime methyl ether,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{NOMe}$ , b. p.  $153$ – $154^\circ$  (decomp.) or  $50$ – $52.5^\circ/15$  mm.,  $D^{20}$  0.9646, a colourless, mobile liquid with a characteristic odour, which reacts with phenylcarbimide to form the phenylurethane,  $\text{NHPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{NOMe}$ , m. p.  $138^\circ$ . Diacetylmonoxime benzyl ether,  $\text{COMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ , b. p.  $130^\circ/12$  mm.,  $D^{20}$  1.0564, prepared from sodium ethoxide, benzyl chloride, and diacetylmonoxime in boiling alcohol, forms a phenylhydrazone,



m. p.  $73^\circ$ , and reacts with ethereal magnesium methyl iodide to yield ultimately trimethylketoloxime benzyl ether,



b. p.  $143^\circ/12$  mm. (decomp.),  $D^{20}$  1.0365, which does not react with

phenylcarbimide. Attempts to hydrolyse the ether by nitrous acid result in complete decomposition, benzaldehyde, benzoic acid, nitric oxide, benzyl nitrate, and benzyl nitrite being produced. C. S.

**Condensation of Formaldehyde.** OSCAR LOEW (*Pflüger's Archiv*, 1909, 128, 282).—A question of priority arising out of Grube's statement (this vol., ii, 328) that H. and A. Euler were the first to obtain sugar by the condensation of formaldehyde in a practically neutral solution. The author had performed similar experiments twenty years earlier. W. D. H.

**Birotation of Dextrose. II.** YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 304—319. Compare Abstr., 1900, i, 127).—The author has studied the influence of temperature, the influence of sodium chloride, both alone and in the presence of hydrochloric acid, and the action of a weak acid on the mutarotation of dextrose. From experiments carried out at 15°, 20°, and 25°, the ratio of the velocities at 25° and 15° is found to be 2·7:1, whilst the velocity constant calculated by Arrhenius' formula for 20° from the constants for 15° and 25° agrees with the observed value (compare Levy, Abstr., 1895, i, 586). In confirmation of the observations of Levy (*loc. cit.*) and Trey (Abstr., 1897, ii, 299), the author finds that the velocity of the mutarotation is diminished by sodium chloride when present to the extent of one-tenth gram-molecule per litre or in greater concentrations. It is found that sodium chloride has no effect on the mutarotation by *N*/15 hydrochloric acid when present to the extent of one-tenth gram-molecule per litre, but that at greater concentrations the catalytic action of the acid is increased (compare Trey).

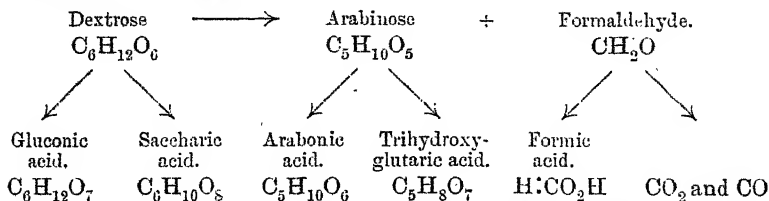
It seemed probable that the catalytic action of an acid being mainly due to hydrogen ions, its presence having diminished the concentration of the hydroxyl ions, a gradual diminution in the concentration of the acid would produce a state in which the action of the hydrogen ions was no longer significant, whilst the concentration of the hydroxyl ions was still far less than in aqueous solution. In such a state the acid would retard the velocity of the mutarotation, whilst further dilution by increasing the concentration of the hydroxyl ions would increase the velocity. A minimum velocity of this nature is actually observed with acetic acid, in *N*/150 solution, and with succinic acid, in *N*/300 solution. E. H.

**The Scission of Sugars. III. Electrolysis of Dextrose.** WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 17, 132—144. Compare Abstr., 1908, i, 715, 764).—The question under investigation was whether synthesis and decomposition of sugar are chemically as well as biologically reversible processes. The electrolysis of dextrose was carried out in dilute sulphuric acid solution in the cold, precautions being adopted to prevent a rise of temperature during electrolysis. Lead electrodes were used, and in presence of an excess of dextrose it was possible to regulate the current so as to have very little gas production at the anode.

After electrolysis, in addition to unaltered dextrose, the solutions contained formaldehyde, formic acid, *d*-arabinose, *d*-arabonic acid,

trihydroxyglutaric acid, gluconic and saccharic acids. Products such as glyceraldehyde, dihydroxyacetone, and lactic acid could not be identified.

The following is considered the most probable scheme to explain the formation of these products :



here the primary process is the decomposition of the dextrose and the secondary process the oxidation to the acids.

E. F. A.

**Crystallised *l*-Ribose.** WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 373—375. Compare Abstr., 1908, i, 9).—Crystallised *l*-ribose has been isolated by converting the ribose syrup obtained by reduction of *l*-ribonolactone into its *p*-bromophenylhydrazone (m. p. 165°), and treatment of this substance with benzaldehyde to liberate *l*-ribose. After the lapse of two months, the syrup thus obtained crystallised. It has m. p. 87°, and  $[\alpha]_D$  in 1.5% aqueous solution = +18.8°. Mutarotation is not exhibited by solutions of this concentration.

A. J. W.

**The Action of Sulphuric and Nitric Acids in the Nitration of Cellulose.** C. NAPIER HAKE and MARCUS BELL (*J. Soc. Chem. Ind.*, 1909, 28, 457—464. Compare Hake and Lewis, Abstr., 1905, i, 512).—The action of mixtures of concentrated sulphuric and nitric acids on cellulose (filter paper) at 10—20° has been studied. In each case a large excess of the acid mixture was used, the ratio of acid mixture to cellulose being usually 50:1 by weight, and after nitration the products were immersed in a large excess of cold water and washed in cold running water until neutral.

Variations of temperature within the limits 0° and 25° and variations in the excess of acid mixture to cellulose (within limits 20—200 of acid to 1 of cellulose) have little or no influence on the formation of sulphuric esters. Similarly, variations in the amount of water show that, within the limits 4—8%, the water contents of the acid have practically no effect. With mixtures of the two acids, a certain amount of sulphuric acid is always found combined in the final product, and the amount increases as the ratio of sulphuric/nitric acid is increased, for example, when the ratio is 1/3 the % combined sulphuric acid in the product is 0.37, and this increases gradually to 6.5 as the ratio is raised to 10/1.

The formation of mixed esters is due to delayed nitration. The cellulose is first partly dissolved or gelatinised by the sulphuric acid and subsequently nitrated.

The nature of the products formed varies with the density of the cellulose; with thick papers, the ratio N/SO<sub>4</sub> in the product is con-

siderably less than when Swedish filter paper is used, and the ratio in this is less than that in the product from cotton wool. J. J. S.

**Morphotrophy of Some Synthetic Compounds.** V. ROSICKÝ (*Zeitsch. Kryst. Min.*, 1909, 46, 357—376).—The ethylenediammonium double salts of iron, manganese, and cadmium described by Grossmann and Schück (Abstr., 1906, i, 630) have been examined goniometrically. The crystals are all triclinic pinakoidal.  $(\text{Fe}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  [ $a:b:c = 0.54737:1:0.42196$ ;  $\alpha = 91^\circ 15\frac{1}{2}'$ ,  $\beta = 94^\circ 18\frac{1}{3}'$ ,  $\gamma = 93^\circ 22'$ ].  $(\text{Mn}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  [ $a:b:c = 0.54646:1:0.42512$ ;  $\alpha = 91^\circ 28\frac{1}{8}'$ ,  $\beta = 94^\circ 53\frac{1}{2}'$ ,  $\gamma = 93^\circ 19\frac{1}{2}'$ ].  $(\text{Cd}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  [ $a:b:c = 0.54594:1:0.43076$ ;  $\alpha = 91^\circ 30\frac{3}{4}'$ ,  $\beta = 94^\circ 31\frac{1}{2}'$ ,  $\gamma = 93^\circ 32\frac{5}{8}'$ ].

Since ethylenediammonium manganosulphate, in the magnitude of its molecular volume and topic axes, comes between the iron and the cadmium salts, the three salts afford an instance in which the crystallographic properties are not periodic functions of the atomic weights of the mutually substituting metals (compare Tutton, Abstr., 1907, ii, 688).

Ethylenediammonium cuprisulphate,  $(\text{Cu}, \text{C}_2\text{H}_{10}\text{N}_2)(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , D 2.128, forms monoclinic prisms [ $a:b:c = 0.86397:1:0.87847$ ;  $\beta = 94^\circ 46'$ ]. The rhombic, pyramidal crystals of the molybdenum compounds,  $[\text{Mo}(\text{SCN})_6(\text{H}_2\text{O})]\text{K}_3\text{C}_2\text{H}_4\text{O}_2$ , D 1.893, and

$[\text{Mo}(\text{SCN})_6(\text{H}_2\text{O})(\text{NH}_3)_3]\text{H}_3\text{C}_2\text{H}_4\text{O}_2$ , D 1.654, have been described by Maas and Sand (Abstr., 1908, i, 397). Ammonium orthosulphovanadate,  $(\text{NH}_4)_2\text{VS}_4$ , forms monoclinic crystals [ $a:b:c = 1.1634:1:1.0165$ ;  $\beta = 90^\circ 27'$ ]. Nef's ethyl 3:6-dimethoxybenzene-1:2:4:5-tetracarboxylate has D 1.276, and forms monoclinic prisms [ $a:b:c = 0.64084:1:0.39365$ ;  $\beta = 105^\circ 15\frac{1}{2}'$ ]. Dihydroxytriphenylacetic acid,  $\text{C}_6\text{H}_5(\text{OH})_2 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$ , D 1.293, is also monoclinic [ $a:b:c = 1.11430:1:0.81194$ ;  $\beta = 120^\circ 26\frac{2}{3}'$ ]. Cuminyltoluidine,

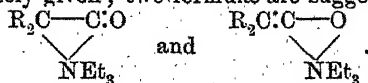
$\text{C}_6\text{H}_4\text{Pr} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , m. p.  $36^\circ$ , D 1.108, triclinic [ $a:b:c = 1.5279:1:1.2793$ ;  $\alpha = 122^\circ 11\frac{1}{2}'$ ,  $\beta = 113^\circ 42\frac{2}{3}'$ ,  $\gamma = 78^\circ 41\frac{1}{2}'$ ]. C. S.

**Lipo-proteins and their Significance in Fatty Degeneration of Cells.** II. Lipo-peptides, their Significance, Synthesis, and Properties. S. BONDI (*Biochem. Zeitsch.*, 1909, 17, 543—552).—The author discusses the possibility of the formation in the organism of condensation products of higher fatty acids and amino-acids. He has prepared lauryl-glycine by condensation of lauryl chloride and glycine, and lauryl-alanine by condensation of lauryl chloride and alanine. The former melted at  $117.5^\circ$ , and the latter not quite sharply at  $103\text{—}104^\circ$ . The glyceryl condensation products are stronger acids than lauric acid itself, as the sodium salts undergo less hydrolytic dissociation; they diffuse through parchment membranes more rapidly than sodium laurate. The condensation products have properties similar to the lipo-proteins, being less soluble than lauric acid, and showing similar staining reaction with Soudan or Scharlach. S. B. S.

Lipo-proteins and their Significance in Fatty Degeneration of Cells. III. Synthesis of Palmityl-glycine and Palmityl-alanine. S. BONDI and TH. FRANKL (*Biochem. Zeitsch.*, 1909, 17, 553—554).—Preparation similar to corresponding lauryl compounds (see preceding abstract). Palmityl-glycine has m. p.  $121^{\circ}$ , and palmityl-alanine, m. p.  $106^{\circ}$  (not quite sharp). S. B. S.

Lipo-proteins and their Significance in Fatty Degeneration of Cells. IV. The Behaviour of Lipo-peptides towards Ferments. S. BONDI and TH. FRANKL (*Biochem. Zeitsch.*, 1909, 17, 555—561).—The sodium salts of lauryl-glycine and lauryl-alanine were used for experiments. Pepsin, trypsin, and the juice from a pancreas fistula were without action. The action of extracts of several organs (from rabbit) was investigated. Only two of these extracts caused hydrolysis of the peptides, namely, those of liver and of kidneys; the latter were the most active. S. B. S.

Ketenium Compounds. EDGAR WEDEKIND and MORIZ MILLER (*Ber.*, 1909, 42, 1269—1275).—It was observed that in the preparation of 1:3-diketotetramethylcyclobutane, an oil having a characteristic odour and b. p. above  $185^{\circ}$  was simultaneously produced (Abstr., 1906, i, 437). This oil has been now obtained in larger quantity, the only difference from the original directions for the preparation being to add a further quantity of triethylamine towards the end of the reaction. From the mixture, dimethylketen-triethylilium,  $\text{OMe}_2\text{C}:\text{CO}, \text{NEt}_3$ , has been isolated as a pale yellow oil, which soon becomes colourless in sunlight, b. p.  $192\text{--}193^{\circ}$ ,  $D_{20}^{25} 0.892$ ,  $n_D 1.440$ . It has an odour resembling menthol, and a determination of its molecular weight in benzene showed it to be unimolecular. Chlorophenylketen-triethylilium,  $\text{ClO}(\text{Ph})\text{C}:\text{CO}, \text{NEt}_3$ , obtained by the interaction of phenylchloroacetyl chloride and triethylamine in light petroleum, the viscous, yellowish-brown mass being distilled at  $138\text{--}142^{\circ}/0.1$  mm., separates from methyl alcohol as a colourless, crystalline powder, m. p.  $51^{\circ}$ , and is unimolecular. Both these compounds differ from Staudinger's keten bases (Abstr., 1907, i, 424) in (1) that he found that the ketens unite with cyclic bases and not with bases of the fatty series; (2) these new compounds contain 1 mol. keten : 1 mol. base, whereas the others have 2 mols. keten : 1 mol. cyclic base; (3) the triethylilium compounds are surprisingly stable, neither boiling dilute acids or alkalis, or even water at  $160^{\circ}$ , decomposing them; hydrochloric acid at  $130^{\circ}$ , however, hydrolyses them with formation of triethylamine hydrochloride and isobutyric acid and mandelic acid respectively. The constitution of these compounds cannot yet be definitely given; two formulæ are suggested:



W. R.

Thioformamide. RICHARD WILLSTÄTTER and THEODOR WIRTH (*Ber.*, 1909, 42, 1908—1922).—Thioformamide,  $\text{CH}_3\text{NS}$ , may be

obtained from formamide and phosphorus pentasulphide by working with small quantities of the materials in the absence of a solvent. With water it forms a *hydrate*,  $\text{CH}_3\text{NS}\cdot\text{H}_2\text{O}$ , which is soluble in ether and can thus be separated readily from unaltered formamide. To obtain the anhydrous compound the ethereal solution is treated with phosphoric oxide, filtered, concentrated, cooled to  $-15^\circ$ , and mixed with light petroleum. It forms a brilliant white, crystalline mass, m. p.  $28-29^\circ$ , but is unstable, and turns yellow in the course of an hour, ultimately yielding a brownish-red syrup. It has a characteristic odour, which becomes more intense as decomposition proceeds, and also has a bitter taste. It appears to react in the tautomeric forms:  $\text{HS}\cdot\text{CH}\cdot\text{NH}\rightleftharpoons\text{S}\cdot\text{CH}\cdot\text{NH}_2$ , and is distinctly acid to litmus. When boiled with water, it yields hydrogen sulphide, with  $\text{conc. alkali}$ , ammonia, and with concentrated sulphuric acid, hydrogen sulphide and sulphur dioxide. It reduces Fehling's solution in the cold, and with silver nitrate yields a precipitate of silver sulphide. It gives precipitates with many salts, and forms additive compounds with bromine and phosphorus trichloride.

With concentrated potassium cyanide solution, it yields crystals of chrysean (Helsing, Abstr., 1899, i, 563), and with benzophenone chloride it gives Tschugaëff's reaction. When heated under reduced pressure, the amide gives dimolecular hydrogen cyanide (iminoformyl cyanide: Nef, Abstr., 1896, i, 71). *Thioformamide hydrochloride*,  $\text{CH}_3\text{NS}\cdot\text{HCl}$ , is obtained as a white, crystalline precipitate by passing hydrogen chloride into a dry ethereal solution of the amide. It is extremely hygroscopic, and, when heated, yields hydrogen sulphide, hydrogen chloride, hydrogen cyanide, carbon disulphide, and carbon monoxide, but no carbon monosulphide.

The amide reacts with chloroacetaldehyde, yielding thiazole (Hantzsch and Popp, Abstr., 1888, 1269), and when an aqueous solution of the platinichloride of this base is warmed, it yields a crystalline precipitate of tetrachlorodithiazole platinum.

A small amount of *thiazoline*,  $\begin{array}{c} \text{CH}_2-\text{S} \\ | \quad \diagup \\ \text{CH}_2\cdot\text{CH} \end{array} \text{N}$ , is formed when the amide is heated with bromoethylamine hydrobromide. It is a colourless oil with an odour recalling those of pyridine and thiophen, and has b. p.  $138-139^\circ$  (corr.).

Alkylated thioformamides have been prepared by the action of phosphorus pentasulphide on alkylated formamides, using Hantzsch's method (Abstr., 1889, 723). *Dimethylthioformamide*,  $\text{S}\cdot\text{CH}\cdot\text{NMe}_2$ , is a pale yellow, strongly refractive oil, b. p.  $96.5-97/12$  mm. or  $227-228/760$  mm. (corr.), and has  $D_4^{20} 1.047$ . It is neutral to litmus, and is not decomposed when heated with phosphoric oxide or zinc chloride. The *methiodide*,  $\text{CHNMe}_2\text{S}\cdot\text{MeI}$ , forms colourless needles, m. p.  $122-123^\circ$ . *Diethylthioformamide*,  $\text{S}\cdot\text{CH}\cdot\text{NEt}_2$ , has b. p.  $116-117/14$  mm. and m. p. below  $0^\circ$ ; the *methiodide* has m. p.  $111-112^\circ$ .

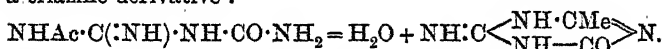
*Thioformylpiperidine*,  $\text{CHS}\cdot\text{C}_5\text{NH}_{10}$ , has b. p.  $148-149/11-12$  mm., and the corresponding *methiodide* crystallises in needles, m. p.  $119-120^\circ$ . *Diphenylthioformamide*,  $\text{CHS}\cdot\text{NPh}_2$ , forms lemon-yellow plates, m. p.  $108-109^\circ$ ; the *methiodide*,  $\text{C}_{14}\text{H}_{14}\text{NSI}$ , has no definite m. p., but decomposes when heated.

J. J. S.

**Tetra-acetamide Compound of Calcium Chloride.** P. I. KUSNETZOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 379—382).—When a mixture of calcium chloride (1 mol.) and acetamide (about 6 mols.) is heated and subsequently cooled, it deposits rosette-shaped aggregates of slender, hatched plates having the composition  $\text{CaCl}_2 \cdot 4\text{COMe} \cdot \text{NH}_2$  and decomposing at 71—72°. The existence of this compound, which is analogous and similar in appearance to the  $\beta$ -tetrahydrate of calcium chloride, was not indicated by the results of Menshutkin (this vol., i, 89).  
T. H. P.

**Condensation of Ethyl Carbamate with Acid Esters.** OTTO DIELS (*Ber.*, 1909, 42, 1853).—The condensation of ethyl carbamate with acid esters (Ruhemann and Priestley, *Trans.*, 1909, 95, 449) has already been applied by Hantzsch (*Abstr.*, 1894, 363) and by Diels (*Abstr.*, 1903, i, 324; 1905, i, 174), and many acylcarbamates have been prepared in this way.  
C. H. D.

**New Derivatives of Guanylcarbamide.** ADRIANO OSTROGOVICH (*Gazzetta*, 1909, 39, i, 540—549).—The interaction of acetyl chloride and guanylcarbamide in a sealed tube at 100° yields *acetylguanylcarbamide hydrochloride*,  $\text{NHAc} \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2 \cdot \text{HCl}$ , which crystallises from water in deep yellow, flattened needles, m. p. 227—228° (decomp.). Attempts to convert the hydrochloride into the free acetylguanylcarbamide result in the conversion of the latter into a triazine derivative:



The change affords a new and excellent method of obtaining triazine bases, which can be synthesised from their elements by way of calcium carbide, calcium cyanamide, cyanoguanidine, guanylcarbamide, acetylguanylcarbamide, and methyliminoketotriazine.

*Guanylcarbamide picrate* crystallises from water in aggregates of yellow laminae, which melt at 280° (decomp.) if plunged into a bath previously heated to that temperature.

*Guanylcarbamide aurichloride*,  $(\text{C}_2\text{H}_6\text{ON}_4 \cdot \text{HCl})_2 \cdot \text{AuCl}_3$ , and two *auribromides*,  $(\text{C}_2\text{H}_6\text{ON}_4 \cdot \text{HBr})_2 \cdot \text{AuBr}_3$  and  $\text{C}_2\text{H}_6\text{ON}_4 \cdot \text{HBr} \cdot \text{AuBr}_3$ , were also prepared.

The action of benzaldehyde on a concentrated sulphuric acid solution of guanylcarbamide sulphate yields benzylideneguanylcarbamide sulphate, which, with ammonia or sodium carbonate, gives *benzylideneguanylcarbamide* (?),  $\text{NH} \begin{array}{c} \text{CHPh} \cdot \text{NH} \\ \text{CO} \text{---} \text{NH} \end{array} \text{C} \text{NH}_2$ , in the form of minute, colourless scales or needles, m. p. 183—184° (decomp.). *Benzylideneguanylcarbamide picrate*, m. p. 211—212° (decomp.), was also prepared.

Benzylidenebiuret can be obtained pure and in theoretical yield by the action of benzaldehyde on a solution of biuret hydrate in concentrated sulphuric acid (compare Biginelli, *Abstr.*, 1894, i, 374, and Schiff, *Abstr.*, 1896, i, 529).  
T. H. P.

**Crystallographic Examination of Some Thiocyno-compounds.** H. STEINMETZ (*Zeitsch. Kryst. Min.*, 1909, 46, 377—379. Compare Maas and Sand, *Abstr.*, 1908, i, 11, 397).—The compound

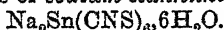
$[\text{Mo}(\text{SCN})_6(\text{H}_2\text{O})(\text{NH}_3)_3]\text{H}_3\cdot 3\text{H}_2\text{O}$  forms brownish-red, twinned, rhombic crystals [ $a:b:c = 0.6134:1:0.8943$ ]. The compound  $[\text{Mo}(\text{SCN})_6(\text{H}_2\text{O})]\text{K}_3\cdot 4\text{H}_2\text{O}$  forms brown or yellow,  $\psi$ -hexagonal crystals [ $a:c = 1:0.6749$ ]. The compound

$[\text{Cr}(\text{SCN})_6(\text{H}_2\text{O})(\text{NH}_3)_3]\text{H}_3\cdot \text{C}_2\text{H}_4\text{O}_2$  forms small, dark red, rhombic crystals [ $a:b:c = 0.72:1:0.6334$ ].

C. S.

**Comparative Crystallographic Examination of Cyanuric Acid and the Acid Product of the Synthesis of Biuret by Ethyl Cyanoacetate, and of their Salts.** E. BILLOWS (*Zeitsch. Kryst. Min.*, 1909, 46, 481—483; from *Riv. Min. Crist. ital.*, 1907, 33, 87—94).—Cyanuric acid forms monoclinic prisms [ $a:b:c = 1.3694:1:1.8502$ ;  $\beta = 106^\circ 41'$ ], whilst its calcium salt crystallises in the triclinic system [ $a:b:c = 1.0928:1:0.5986$ ;  $a = 81^\circ 10'$ ,  $\beta = 87^\circ 16'$ ,  $\gamma = 103^\circ 38'$ ]. The acid product of the synthesis of biuret by ethyl cyanoacetate closely resembles cyanuric acid in its composition and behaviour, but differs greatly in its crystalline form; it belongs to the triclinic system [ $a:b:c = 0.9850:1:0.5552$ ;  $a = 92^\circ 11'$ ,  $\beta = 114^\circ 1'$ ,  $\gamma = 76^\circ 61'$ ], whilst its calcium salt is monoclinic, the crystals, however, being too small for measurement. C. S.

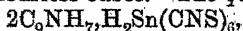
**Stannithiocyanates.** RUDOLF WEINLAND and ERNST BAMES (*Zeitsch. anorg. Chem.*, 1909, 62, 250—264).—The only thiocyanates of a quadrivalent metal known, other than those containing oxygen, are the platinithiocyanates. It is now found that sodium stannichloride,  $\text{Na}_2\text{SnCl}_6\cdot 6\text{H}_2\text{O}$ , reacts with sodium thiocyanate in alcohol, forming colourless prisms of *sodium stannithiocyanate*,



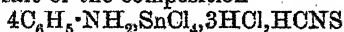
The salt may also be prepared in aqueous solution. The *potassium* salt,  $\text{K}_2\text{Sn}(\text{CNS})_6\cdot 4\text{H}_2\text{O}$ , forms colourless plates or prisms. The *magnesium* salt,  $\text{MgSn}(\text{CNS})_6\cdot 6\text{H}_2\text{O}$ , hygroscopic leaflets; *calcium* salt,  $\text{CaSn}(\text{CNS})_6\cdot 7\text{H}_2\text{O}$ , tablets, and *strontium* salt,  $\text{SrSn}(\text{CNS})_6\cdot 12\text{H}_2\text{O}$ , glistening needles, are also described.

The organic salts are prepared either by dissolving stannichlorides of organic bases in 10% thiocyanic acid solution, or by mixing solutions of sodium stannichloride and sodium thiocyanate with a nitric acid solution of the organic base.

*Pyridine stannithiocyanate*,  $2\text{C}_5\text{NH}_5\cdot \text{H}_2\text{Sn}(\text{CNS})_6$ , may be recrystallised from acetone in colourless cubes. The *quinoline* salt,



forms a white, microcrystalline powder; the *dimethylaniline* salt,  $2\text{C}_6\text{H}_5\text{NMe}_2\cdot \text{H}_2\text{Sn}(\text{CNS})_6$ , forms pale yellow, quadratic leaflets. The *pyridine sodium* salt,  $2\text{C}_5\text{NH}_5\cdot \text{H}_2\text{Sn}(\text{CNS})_6\cdot \text{NaCNS}$ , forms microscopic cubes. An *aniline* salt of the composition



is obtained in colourless, double pyramids when aniline stannichloride is dissolved in thiocyanic acid.

The new salts are more readily decomposed by water than the stannichlorides. Silver nitrate precipitates the whole of the thiocyanate from their aqueous solutions. The co-ordination number of the simpler salts is 6; the proper formulation of the more complex aniline and pyridine sodium salts is still undetermined. C. H. D.

**Reaction between Ferric Chloride and Potassium Ferri-cyanide.** YOGORO KATO (*Mem. Col. Sci. Eng. Kyōto*, 1908, i, 352—374).—Although ferric chloride and potassium ferrocyanide only give a reddish-brown colour when mixed in dilute aqueous solution, it has been shown by Spring (*Bull. Acad. Roy. Belg.*, 1892, [iii], 34, 255) that a deep blue precipitate, with evolution of chlorine, is produced when very concentrated solutions of ferric chloride are used, and he ascribed this to a change in the stability of ferric chloride with change of concentration. It is now shown that a blue colour is produced even in dilute solutions of the reagents when the reaction takes place in concentrated solutions of many salts, and various explanations of this observation are suggested and tested.

The salts of metals having the same valency have, in solutions of equal concentration, nearly equal capacity for promoting the reaction, but it takes place in a more dilute solution in the case of the salts of metals of higher valency. It is not probable that the reaction is connected with the elimination of chlorine according to the equation:  $2\text{FeCl}_3 = 2\text{FeCl}_2 + \text{Cl}_2$ , as ferric nitrate and sulphate behave very like ferric chloride. Neither is the suggestion of Spring, that the decomposition potential of ferric chloride into ferrous chloride and chlorine varies with the concentration, an adequate explanation of the observations, as experiment shows that the decomposition potential of ferric chloride does not vary greatly with the concentration. The final conclusion is drawn that the reaction is connected with the precipitation of colloidal Prussian blue by the salts. G. S.

**Action of Hydrogen Sulphide on Imino-ethers.** MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 285—289).—The action of hydrogen sulphide on imino-ethers is found to be analogous to that of water on their hydrochlorides (Pinner, *Abstr.*, 1883, 730), and to that of hydrogen sulphide on the substituted amidines (Bernthsen, *Abstr.*, 1878, 70), the imide group being replaced by sulphur and a  $\beta$ -thiocarboxylic ester formed. When dry hydrogen sulphide is passed into an ethereal solution of ethyl iminoacetate (Pinner, *Abstr.*, 1883, 1089), there is formed *ethyl  $\beta$ -thionacetate*,  $\text{CH}_3\cdot\text{CS}\cdot\text{OEt}$ , a yellow, mobile liquid having a very unpleasant odour, which reacts violently with concentrated nitric acid, forming ethyl acetate, but does not yield the thio-acid on saponification. If the ethereal solution into which hydrogen sulphide has been passed is kept, the thionacetate is completely transformed into thioacetamide. *Ethyl  $\beta$ -thionpropionate*, prepared similarly, is a yellow liquid, b. p. 128—130°, having a very disagreeable odour and similar properties to those of ethyl  $\beta$ -thionacetate, except that it does not form thiopropionamide.

By passing dry hydrogen sulphide into an ethereal solution of ethyl iminobenzoate, thiobenzamide and *ethyl  $\beta$ -thionbenzoate*,  $\text{C}_6\text{H}_5\cdot\text{CS}\cdot\text{OEt}$ , are formed. The latter is a yellow liquid having a very disagreeable odour, and properties analogous to those of the other two thio-esters. It changes into thiobenzamide when kept in contact with alcoholic ammonia. E. H.

**Reactions of Ethyl Diazoacetate.** ANTON LOOSE (*J. pr. Chem.*, 1909, 79, 505—510).—I. Ethyl diazoacetate reacts slowly with boiling *d*-pinene, yielding a substance,  $\text{C}_{14}\text{H}_{22}\text{O}_2$ , obtained as a colourless

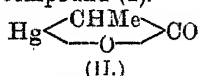
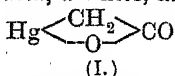
liquid, b. p. 140—150°/15 mm. It is converted by boiling 15% aqueous sodium hydroxide into another substance, obtained as a colourless liquid, b. p. 170—180°/15 mm., having a pine-like odour.

II. Ethyl diazoacetate decomposes when its solution in light petroleum (b. p. 98—100°) is warmed in the presence of platinum, mercury, or aluminium, yielding ethyl pyrazoline-3:4:5-tricarboxylate. When copper-bronze (Kahlbaum's naturkupfer C) is employed, however, 70% of the product of the reaction is ethyl fumarate. The condensation product of pinene with ethyl diazoacetate just described is more rapidly obtained by using copper-bronze as a catalyst.

W. H. G.

**Preparation of Iron Salts of Arsenitartaric and Arsenicitric Acids.** CARL SORGER (D.R.-P. 208711).—The double alkali ferrous salts of arsenitartaric and arsenicitric acids are soluble substances, and are thirty-five times less poisonous than arsenious acid. *Ferrous arsenitartrate*, greyish-white powder soluble in cold dilute sodium hydroxide, is prepared by adding successively arsenic acid and ferrous sulphate to a solution of sodium tartrate and sodium carbonate. *Ferrous arsenicitrate* is similarly prepared by using ferric chloride instead of ferrous sulphate; the corresponding ferric salts are produced. *Sodium ferric arsenitartrate*, a deep yellow salt, is precipitated by adding ferric chloride to a concentrated solution of tartaric and arsenic acids dissolved in excess of sodium carbonate. F. M. G. M.

**[Preparation of the Mercury Derivatives of Fatty Acids.]** WALTHER SCHOELLER and WALTHER SCHRAUTH (D.R.-P. 208634).—When methyl malonate and mercuric oxide are suspended in water and shaken together for twelve hours, a white compound, *methyl mercuridimalonate*,  $\text{Hg}[\text{CH}(\text{CO}_2\text{Me})_2]_2$ , results. This substance, when shaken with aqueous sodium hydroxide, undergoes further change, and the solution, when acidified, gives rise to the *anhydride of hydroxy-mercuriacetic acid*, a white, amorphous compound (I).



Methyl methylmalonate gives the corresponding *anhydride of hydroxymercuripropionic acid* (II). The corresponding *hydroxy-mercuributyric acid* is formed from mercuric oxide and methyl ethylmalonate. F. M. G. M.

**Crystalline Forms of Some Benzene Derivatives.** E. REPOSSI (*Zeitsch. Kryst. Min.*, 1909, 46, 402—407).—The following data are given:

2:5-Dibromonitrobenzene: triclinic [ $a:b:c = 1.3854:1.07879$ ;  $\alpha = 87^\circ 29'$ ,  $\beta = 114^\circ 35'$ ,  $\gamma = 83^\circ 26'$ ]. 2-Chloro-5-bromonitrobenzene: triclinic [ $a:b:c = 1.3823:1.08196$ ;  $\alpha = 86^\circ 30'$ ,  $\beta = 114^\circ 29'$ ,  $\gamma = 82^\circ 20'$ ]. 5-Chloro-2-bromonitrobenzene: triclinic [ $a:b:c = 1.4159:1.08157$ ;  $\alpha = 87^\circ 17'$ ,  $\beta = 113^\circ 47'$ ,  $\gamma = 82^\circ 25'$ ]. 2:5-Dichloronitrobenzene: triclinic [ $a:b:c = 1.4385:1.08223$ ;  $\alpha = 87^\circ 18'$ ,  $\beta = 114^\circ 17'$ ,  $\gamma = 82^\circ 37'$ ]. 3-Bromo-2-iodonitrobenzene: monoclinic [ $a:b:c = 0.6342:1.05680$ ;  $\beta = 105^\circ 430''$ ]. 2:3-Dibromonitrobenzene: monoclinic [ $a:b:c =$

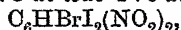
1.0309 : 1.02824 ;  $\beta = 99^\circ 51' 30''$ ]. 1:2:3-Tribromobenzene: monoclinic [ $a:b:c = 1.5490 : 1.18516$  ;  $\beta = 113^\circ 7' 30''$ ]. The first four compounds are isomorphous. C. S.

**Crystalline Forms of Some Benzene Derivatives.** ETTORE ARTINI (*Zeitsch. Kryst. Min.*, 1909, 46, 407—414).—The following crystallographic data are given:

4:6-Di-iodo-1:3-dinitrobenzene: rhombic, bipyramidal [ $a:b:c = 2.1859 : 1.07084$ ]. 3:5-Dichloro-1:2-dinitrobenzene: ditetragonal, bipyramidal [ $a:c = 1.19767$ ]. 2-Bromo-6-nitroaniline: monoclinic, prismatic [ $a:b:c = 1.2799 : 1.03809$  ;  $\beta = 111^\circ 54'$ ]. 2-Bromo-5-nitroacetanilide: monoclinic, prismatic [ $a:b:c = 3.3702 : 1.12522$  ;  $\beta = 102^\circ 57'$ ]. 2:4-Dichloro-5-nitroaniline: monoclinic, prismatic [ $a:b:c = 2.1321 : 1.30222$  ;  $\beta = 106^\circ 33'$ ]. 2-Chloro-4-bromo-5-nitroaniline: monoclinic, prismatic [ $a:b:c = 2.1367 : 1.30297$  ;  $\beta = 107^\circ 10'$ ]. 4-Chloro-2-bromo-5-nitroaniline: monoclinic, prismatic [ $a:b:c = 2.1525 : 1.29625$  ;  $\beta = 105^\circ 44'$ ]. 2:4-Dibromo-5-nitroaniline: monoclinic, prismatic [ $a:b:c = 2.1598 : 1.30212$  ;  $\beta = 106^\circ 9'$ ]. 2:4-Dichloroacetanilide: monoclinic, prismatic [ $a:b:c = 0.8252 : 1.06773$  ;  $\beta = 102^\circ 34'$ ]. 2-Chloro-4-bromoacetanilide: monoclinic, prismatic [ $a:b:c = 0.8152 : 1.06669$  ;  $\beta = 103^\circ 18'$ ]. 4-Chloro-2-bromoacetanilide: monoclinic, prismatic [ $a:b:c = 0.8230 : 1.07088$  ;  $\beta = 102^\circ 11'$ ]. 2:4-Dibromoacetanilide: monoclinic, prismatic [ $a:b:c = 0.8135 : 1.06903$  ;  $\beta = 103^\circ 5'$ ].

C. S.

**2-Bromo-1:3:5-tri-iodo-4:6-dinitrobenzene.** CHARLES LORING JACKSON and H. E. BIGELOW (*Ber.*, 1909, 42, 1868—1869).—2-Bromo-1:3:5-tri-iodobenzene,  $C_6H_2BrI_3$ , obtained from *s*-tri-iodoaniline, has m. p.  $139^\circ$ , and reacts with fuming nitric acid, yielding the dinitro-derivative,  $C_6BrI_3(NO_2)_2$ , m. p.  $292^\circ$ . When the dinitro-compound is left in contact with an alcoholic solution of ethyl sodiomalonate, the chief product is 2-bromo-1:3-di-iodo-4:6-dinitrobenzene,



m. p.  $187^\circ$ , ethyl ethanetetra-carboxylate being also formed. The behaviour of the nitro-compound is thus analogous to that of 1:3:5-tri-iodo-4:6-dinitrobenzene (*Abstr.*, 1904, i, 861). J. J. S.

**Preparation of Benzenesulphonyl Chloride.** RUDOLF PUMMERER (*Ber.*, 1909, 42, 1802—1804).—Benzenesulphonyl chloride is conveniently prepared by the action of chlorosulphonic acid on benzene. It is advisable to work up large quantities in one operation at a low temperature, and use a large excess of chlorosulphonic acid. The acid is cooled to  $-15^\circ$ , stirred, and benzene allowed to drop in slowly during three to four hours; the mixture is poured on to ice, the oil separated, and distilled in a vacuum. E. F. A.

**Preparation of Benzenesulphonyl Chloride.** FRITZ ULLMANN (*Ber.*, 1909, 42, 2057—2058).—In the preparation of benzenesulphonyl chloride from benzene and chlorosulphonic acid, the low yield obtained by Pummerer (preceding abstract) is due to the

employment of too low a temperature. At 15–20° a yield of 62% is obtained. After an hour, the mass is poured on to ice, extracted with ether, and the residue, after evaporation of the ether, distilled under reduced pressure. The chloride passes over, leaving a residue of sulphobenzide. C. H. D.

**Catalytic Reactions at High Temperatures and Pressures. XVIII. Reduction of Fluorene, Acenaphthene, and Retene in Presence of Nickel Oxide.** WLADIMIR N. IPATIEFF (*Ber.*, 1909, 42, 2092–2096).—Polynuclear aromatic hydrocarbons, which are only incompletely reduced by the ordinary methods, undergo complete reduction with hydrogen under high pressure in presence of nickel oxide. Fluorene is reduced in two stages when heated at 285° under 120 atmospheres, the first product being decahydrofluorene, which is afterwards converted into perhydrofluorene,  $C_{13}H_{22}$ . Similarly, acenaphthene yields tetra- and deca-hydroacenaphthene.

Retene first yields dodecahydroretene, and, on further reduction, *perhydroretene*,  $C_{13}H_{32}$ , an oil, b. p. 300–315°. It is not identical, as had been suspected, with fichtelite, the hydrocarbon found together with retene in Bavarian peat (Bamberger, *Abstr.*, 1889, 714).

C. H. D.

**2:6-Dinitro-4-amino-*m*-xylene.** RAFFAELE MALTESE (*Gazzetta*, 1909, 39, i, 517–520).—2:6-Dinitro-4-benzoylamino-*m*-xylene,  $NHBz \cdot C_6HMe_2(NO_2)_2$ , obtained by nitrating 2-nitro-4-benzoylamino-*m*-xylene (*Abstr.*, 1904, i, 307), forms small, shining laminae, m. p. 244°.

2:6-Dinitro-4-amino-*m*-xylene,  $NH_2 \cdot C_6HMe_2(NO_2)_2$ , crystallises from aqueous alcohol in orange-yellow needles, and from alcohol in hard, dark red prisms, m. p. 145°. T. H. P.

**Imino-chlorides of Oxalic Acid. II.** RUDOLPH BAUER (*Ber.*, 1909, 42, 2111–2118).—It has been shown previously (*Abstr.*, 1907, i, 603) that diphenyl- and the three ditolyl-oxalimino-chlorides are converted by concentrated sulphuric acid into isatin and methylisatins respectively. The object of the present investigation was to prepare methoxyisatins by similar means, but it is found that di-*p*-anisylloxalimino-chloride is converted only to a very slight extent, whilst the *o*-compound is not converted at all, into the corresponding methoxyisatins; in both cases the chief product is an oxaloanisididedisulphonic acid.

Heating phenol ethers with *N*-hydrochloric acid under pressure at 175–180° is recommended as a good method of hydrolysing these compounds.

**Di-*p*-anisylloxalimino-chloride**,  $C_2Cl_2 \cdot (N \cdot C_6H_4 \cdot OMe)_2$ , prepared by treating a solution of oxalo-*p*-aniside in benzene with phosphorus pentachloride, crystallises in yellow needles, m. p. 150°. When treated with concentrated sulphuric acid, it yields oxalo-*p*-anisididedi-*o*-sulphonic acid,  $C_2O_2[NH \cdot C_6H_3(SO_3H) \cdot OMe]_2$ , which crystallises with  $8H_2O$  in slender, white needles and prisms, m. p. 261° (decomp.), and is converted by boiling 30% sulphuric acid into 4-amino-1-methoxybenzene

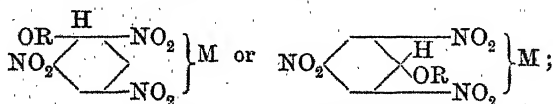
2-sulphonic acid (compare this vol., i, 470). 5-Methoxyisatin-3-phenylhydrazone,  $C_{15}H_{13}O_2N_3$ , crystallises in dark yellow, hair-like needles, m. p.  $219^\circ$ .

The following compounds are prepared by methods similar to those just described. Di-o-anisylloxalimino-chloride,  $C_{16}H_{14}O_2N_2Cl_2$ , crystallises in small, yellow, rhombic plates, m. p.  $101^\circ$ . Oxalo-o-anisididedi-sulphonic acid,  $C_{16}H_{16}O_{10}N_2S_2$ , forms colourless, hair-like needles, m. p.  $271^\circ$  (decomp.); the ammonium salt,  $C_{16}H_{22}O_{10}N_4S_2 \cdot 2H_2O$ , crystallises in white prisms.

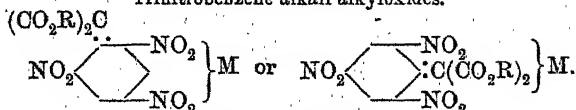
It is shown in conclusion that the methylisatin derived from di-m-tolyloxalimino-chloride (*loc. cit.*) is identical with that described by Findelee (Abstr., 1906, i, 43); further, this compound is 6-methylisatin, since it is oxidised by chromic acid to *m*-homoisatoic acid. 6-Methylisatin has m. p.  $182^\circ$ , and not  $165^\circ$  as given previously; the phenylhydrazone,  $C_{15}H_{13}ON_3$ , forms golden-yellow, hair-like needles, m. p.  $236^\circ$ . 6-Methylisatoxime,  $C_9H_8O_2N_2$ , crystallises in yellow leaflets, m. p.  $235^\circ$ .

W. H. G.

The Chromophore of Salts from Polynitrobenzene Derivatives. ARTHUR HANTZSCH and NORMAN PICTON (*Ber.*, 1909, 42, 2119—2126).—Although 2:4:6-trinitrobenzene, ethyl 2:4-dinitrophenylmalonate, and ethyl 2:4:6-trinitrophenylmalonate are practically colourless, nevertheless the compounds of the first-named substance with alkali alkyl oxides and the salts of the two esters are intensely coloured, and give absorption spectra which are extremely similar, from which fact the conclusion is drawn that they all possess the same chromophoric group. Since the salts obtained by the addition of potassium methoxide to mononitro-compounds, such as nitroanthracene, are colourless, it is evident that the colour of the salts derived from the polynitro-compounds is due to the combined action of two nitro-groups. Definite structural formulæ cannot yet be assigned to these substances, but omitting ethylene linkings they may be represented by the following formulæ:



Trinitrobenzene alkali alkyl oxides.



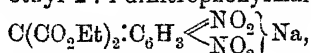
Salts of trinitrophenylmalonic ester.

In agreement with the view that the chromo-salts have the above quinonoid formulæ is the fact that the deep brownish-red silver salt of ethyl trinitrophenylmalonate yields with ethyl iodide a brown, oily, unstable ester, which undoubtedly contains the analogous chromophoric group,  $C_6H_2(NO_2)_2\{Et\}$ , and passes slowly into a crystalline, orange-coloured, stable isomeride. This stable ester, since it is

coloured, cannot be the true ethyl ester of trinitrophenylethylmalonic acid,  $C_6H_2(NO_2)_3 \cdot CEt(CO_2Et)_2$ , but is undoubtedly the ethyl derivative of the enolic form of the ester,  $C_6H_2(NO_2)_3 \cdot C(CO_2Et) : C(OEt)_2$ .

2 : 4 : 6-Trinitrobenzene can be obtained as snow-white leaflets; the compound with sodium methoxide yields with acetone the substance,  $C_6H_3(NO_2)_3 \cdot MeONa \cdot \frac{1}{2} COMe_2$ , which crystallises in small, dark green needles.

The sodium salt of ethyl 2 : 4-dinitrophenylmalonate,



crystallises in long, reddish-brown prisms; the silver salt is very unstable.

The potassium salt of ethyl 2 : 4 : 6-trinitrophenylmalonate crystallises in small, brownish-red needles. The silver salt,  $C_{12}H_{12}O_{10}N_3Ag$ , is a reddish-brown powder, and when treated with ethyl iodide yields the chromo-ester,  $C(CO_2Et)_2 \cdot C_6H_2(NO_2)_3 \begin{smallmatrix} \nwarrow NO_2 \\ \nearrow NO_2 \end{smallmatrix} Et$ , a brown oil which passes slowly into the oxygen ester,  $C_6H_2(NO_2)_3 \cdot C(CO_2Et) : C(OEt)_2$ , orange-yellow crystals, m. p.  $81^\circ$ .

All attempts to prepare the ester,  $C_6H_2(NO_2)_3 \cdot CEt(CO_2Et)_2$ , were unsuccessful.

W. H. G.

**Combination of Picric Acid and  $\beta$ -Naphthol.** LOUIS PELET-JOLIVET and TH. HENNY (*Bull. Soc. chim.*, 1909, [iv], 5, 623—626).—Sisley has shown that picric acid combines with certain hydrocarbons and with  $\beta$ -naphthol more readily in presence of acids than in neutral solution, and similarly that certain dyes, which will not dye silk in dilute solution, do so if acid is added, and argues from analogy that if the formation of picrate of  $\beta$ -naphthol is a chemical combination, so also must be the fixation of dye by a tissue (*Bull. Soc. chim.*, 1908, October).

In the present paper it is shown (1) that more  $\beta$ -naphthol picrate is formed in acid than in neutral solution; (2) that the quantity formed depends on the number of H-ions present, and (3) that in neutral solution the formation of some picrate is due to the  $\beta$ -naphthol becoming positively charged, due to the H-ions present. These results show that the combination of picric acid with  $\beta$ -naphthol takes place according to the law of adsorption. Adsorption may be the result of partial dissociation of a chemical compound in aqueous solution.

T. A. H.

**Oxidation of Quinol by the Catalysis of Carbon.** MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 386—390. Compare Hofmann, *Ber.*, 1874, 7, 530; Cazeneuve, *Abstr.*, 1890, 690; Freundlich, *Abstr.*, 1907, ii, 155).—When charcoal and quinol moistened with water are rubbed together in a mortar, or when a small quantity of charcoal is added to a 3% aqueous or alcoholic solution of quinol, oxidation takes place, and green crystals of quinhydrone separate. In ethereal solution only a slight oxidation occurs, whilst in aqueous and alcoholic solution it proceeds at about equal rates. The oxidation is not due to the oxygen contained in the

charcoal, since it does not occur in the absence of air, and the view that it is due to the oxygen of the air is supported by the observation that the greater the surface of the quinol solution the greater is the effect. The rate of oxidation is increased by raising the temperature, particularly in ethereal solution.

The purest form of animal charcoal (from Merck) was used, whilst finely powdered wood charcoal was found to have a similar, but very feeble, catalytic action.

E. H.

**Bismuth Salts of Brominated Catechols.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 207544).—Bismuth tribromophenoxide employed medicinally under the name of "Xeroform" is neither tasteless nor odourless, and a more satisfactory medicament is obtained by employing brominated catechols.

The bismuth derivative of tetrabromocatechol, a yellow powder, is produced by adding an acid solution of bismuth nitrate to alkaline tetrabromocatechol or by introducing precipitated bismuth hydroxide into an alcoholic solution of catechol. Similar products are obtainable from di- and tri-bromocatechols.

F. M. G. M.

**New Derivatives of Catechol. Preparation of Phenylethylenecatechol.** I. LAZENEC (*Bull. Soc. chim.*, 1909, [iv], 5, 509—511. Compare this vol., i, 488).—Moureu found (*Abstr.*, 1899, i, 494) that *o*-hydroxyphenoxyacetal could be dehydrated by the usual agents, such as phosphoric anhydride, yielding ethylenecatechol, but this method is not available in the case of *o*-hydroxyphenoxyacetophenone, which is, however, readily dehydrated by careful heating under reduced pressure. The product of this reaction is phenylethylenecatechol,  $C_6H_4 \begin{smallmatrix} & O \cdot CH \\ & | \\ O \cdot CPh \end{smallmatrix}$ , m. p. 73°, which crystallises in colourless lamellae from methyl alcohol. The dibromide could not be isolated in a free state, but on heating during eight hours in water with calcium carbonate is decomposed, yielding phenylglyoxal and catechol, which from analogy to Moureu's results (*loc. cit.*) establishes the constitution of the parent substance.

T. A. H.

**Preparation of Pyrogallol from 2:6-Dichloro-4-sulphonic Acid.** AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 207374).—2:6-Dichlorophenol-4-sulphonic acid when heated with 40% aqueous potassium hydroxide at 150—160° yields potassium pyrogallol-5-sulphonate, which on heating at 200° in slightly acidified solution gives rise to pyrogallol.

F. M. G. M.

**Crystallographic Examination of Some Organic Additive Compounds.** GIOVANNI BOERIS (*Zeitsch. Kryst. Min.*, 1909, 46, 472—474. From *Mem. Accad. Sci. Bologna*, 1907, (vi, a), 4, 343).—The additive compound, m. p. 76—77°, of isoapiole and *s*-trinitrobenzene separates from a mixture of alcohol and ether in monoclinic crystals [ $\alpha : \beta : \gamma = 0.9090 : 1.04194$ ;  $\beta = 90^\circ 57'$ ]; The additive compound, m. p. 152°, of naphthalene and *s*-trinitrobenzene forms monoclinic crystals [ $\alpha : \beta : \gamma = 2.3170 : 1.40961$ ;  $\beta = 96^\circ 36'$ ], isomorphous with

the additive compound of naphthalene and picric acid. Naphthalene and picryl chloride form an additive compound,  $C_{10}H_8 \cdot C_6H_2(NO_2)_3Cl$ , m. p. 95—96°, which crystallises in the triclinic system [ $a:b:c = 0.4940:1:0.4455$ ;  $\alpha = 100^\circ 59'$ ,  $\beta = 93^\circ 54'$ ,  $\gamma = 85^\circ 28'$ ]. Isomorphous with this is the additive compound of naphthalene and trinitrotoluene [ $a:b:c = 0.4891:1:0.4839$ ;  $\alpha = 99^\circ 16'$ ,  $\beta = 94^\circ 35'$ ,  $\gamma = 85^\circ 35'$ ]. The methyl group and the halogen apparently exert the same crystallographic influence; Jaeger uses the same conception to explain the isomorphism of 2:3:5- and of 3:4:5-tribromotoluene. C. S.

**Action of Aromatic Mercaptides on Ethyl  $\alpha$ -Chloroacetate.** HERMANN FINGER and O. HEMMETER (*J. pr. Chem.*, 1909, 79, 449—451).—Sodium phenylmercaptide and ethyl  $\alpha$ -chloroacetate interact in equivalent quantities in alcoholic solution, yielding diphenyl disulphide and ethyl diacetylsuccinate, thus:  $2PhSNa + 2CMeO \cdot CHCl \cdot CO_2Et = 2NaCl + PhS \cdot SPh + \begin{matrix} CHAc \cdot CH \cdot CO_2Et \\ | \\ CHAc \cdot CH \cdot CO_2Et \end{matrix}$

Sodium *p*-tolylmercaptide and ethyl  $\alpha$ -chloroacetate interact in an analogous manner. W. H. G.

**4-Amino-1-methoxybenzene-2-sulphonic Acid.** RUDOLF BAUER (*Ber.*, 1909, 42, 2106—2111).—4-Amino-1-methoxybenzene-2-sulphonic acid has been prepared for purposes of identification (compare this vol., i, 466).

*Dipotassium 4-benzylidene-amino-1-phenol-2-sulphonate,*



prepared by the condensation of benzaldehyde and potassium 4-amino-phenol-2-sulphonate in alcoholic solution, crystallises in greenish-yellow needles and leaflets. It is converted by carbon dioxide in aqueous solution into the *potassium* salt,  $CHPh \cdot N \cdot C_6H_3(OH) \cdot SO_3K$ , which crystallises in yellowish-white prisms. Both salts are instantly decomposed by acids into benzaldehyde and aminophenolsulphonic acid.

*Potassium benzylidene-*p*-anisidine-2-sulphonate*,  $C_{14}H_{12}O_4NSK \cdot H_2O$ , is obtained by the action of methyl sulphate on an alkaline solution of the dipotassium salt just described; it crystallises in yellowish-white leaflets, and when decomposed by acids yields 4-amino-1-methoxybenzene-2-sulphonic acid,  $\begin{matrix} CH \cdot C(OMe) \cdot C \cdot SO_3H \\ | \\ CH \cdot C(NH_2) \cdot CH \end{matrix}$ , which crystallises with

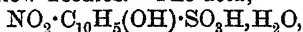
$2H_2O$  in long, colourless prisms and needles, and commences to carbonise at 320°. The latter substance when diazotised yields 4-diazoanisole-2-sulphonic acid,  $OMe \cdot C_6H_3 \cdot \begin{matrix} SO_2 \\ \diagup \quad \diagdown \\ N \cdot N \end{matrix} \cdot O$ , which crystallises in almost colourless, rectangular plates and prisms, and explodes slightly at 191° without melting.

Large quantities of 4-amino-1-methoxybenzene-2-sulphonic acid are best prepared by sulphonating *p*-anisidine with fuming sulphuric acid.

W. H. G.

**Naphthol Yellow-S.** HERMANN FINGER [with E. BRETSCH and W. ZEH] (*J. pr. Chem.*, 1909, 79, 441—445).—It is shown that the com-

pound obtained by reducing naphthol yellow-S with stannous chloride and hydrochloric acid (compare Lauterbach, Abstr., 1882, 63) is 2-nitro-4-amino- $\alpha$ -naphthol-7-sulphonic acid. When treated with aqueous-alcoholic hydrochloric acid and amyl nitrite, it yields the corresponding diazo-derivative,  $\text{OH}\cdot\text{C}_{10}\text{H}_4(\text{NO}_2)\text{SO}_3\text{H}$ , obtained as small, brown crystals, which, when boiled with absolute alcohol and copper powder and subsequently with water, yields copper 2-nitro- $\alpha$ -naphthol-7-sulphonate,  $[\text{NO}_2\cdot\text{C}_{10}\text{H}_3(\text{OH})\cdot\text{SO}_3]_2\text{Cu}\cdot 5\text{H}_2\text{O}$ , crystallising in small, greenish-yellow needles. The acid,



crystallises in slender, lemon-yellow needles, and is reduced by stannous chloride and hydrochloric acid to 2-amino- $\alpha$ -naphthol-7-sulphonic acid,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_3(\text{OH})\cdot\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$ , crystallising in colourless needles. An alkaline solution of the latter substance becomes green when exposed to the air; the sodium salt, when acted on by nitroso-*m*-dimethylaminophenol hydrochloride in aqueous solution, yields an oxazine dye, which forms small, brass-yellow crystals, and dyes wool, but not cotton, an intense blue.

W. H. G.

Modifications of Anthesterol and its Benzoate. TIMOTHÉE KLOBE, *Compt. rend.*, 1909, 148, 1272—1274. Compare Abstr., 1902, i, 165).—Like certain other cholesterols, anthesterol exists in several modifications; these are prepared by hydrolysis of the corresponding benzoates. The  $\alpha$ -benzoate, m. p. 284—286° (*loc. cit.*), has  $[\alpha]_D + 64.36^\circ$  in carbon tetrachloride. On hydrolysis it gives  $\alpha$ -anthesterol, m. p. 221—223°,  $[\alpha]_D + 54.1^\circ$  in xylene. The  $\beta$ -benzoate, m. p. 230—235°, crystallises in lamellae, and has  $[\alpha]_D + 68.8—71.7^\circ$  in carbon tetrachloride. On hydrolysis it forms  $\beta$ -anthesterol. When heated on the Maquenne block this melts at 160—164°, then solidifies, and again melts at 190—195°. It has  $[\alpha]_D + 48.3^\circ$  in xylene, and 56.8° in ethylene dibromide. The  $\gamma$ -benzoate crystallises with  $\frac{1}{2}\text{H}_2\text{O}$  in spherical aggregates, m. p. 240—250°,  $[\alpha]_D + 66.7^\circ$ . Boiling alcohol transforms it into the  $\beta$ -benzoate.

Both  $\alpha$ - and  $\beta$ -anthesterol spontaneously change into a more stable modification,  $\delta$ -anthesterol, m. p. 150—160°;  $[\alpha]_D + 44.7^\circ$  in xylene.

W. O. W.

Polynaphthenic Acids. II. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 345—353. Compare this vol., i, 154).—Oxidation of the fraction of naphtha, b. p. 164—166°/753 mm., by means of air in presence of powdered sodium hydroxide yields an acid,  $\text{C}_{24}\text{H}_{24}\text{O}_4$ , D 1.025, containing two hydroxyl groups and one carboxyl group.

Oxidation in a similar manner of synthetic heptanaphthene (dimethylcyclopentane), obtained by reducing toluene by means of hydriodic acid in a sealed tube at 240—260°, yields a syrupy acid, the character of which was not determined.

No definite oxidation products were obtained with the fractions of Grosny naphtha: (1) b. p. 144—146°, D 0.765, containing trimethyl-

and methylethyl-cyclohexanes; and (2) b. p. 128—129°, which should correspond with one of the octanaphthenes.

The main product of the oxidation of cymene by means of air in presence of alkali consists of cuminic acid. Menthane apparently yields a mixture of naphthenic and polynaphthenic acids.

These results are discussed in relation to the structure of the benzene nucleus (compare Obermiller, Abstr., 1907, i, 200; Vidal, Abstr., 1907, i, 1020).

T. H. P.

**Catalytic Reactions at High Temperatures and Pressures.**  
**XIX. Reduction of Aromatic Acids in Presence of Nickel Oxide and Cupric Oxide.** WLADIMIR N. IPATIEFF (*Ber.*, 1909, 42, 2097—2102).—Since aromatic acids are not reduced by hydrogen in presence of cupric oxide, whilst ethylene linkings are so reduced (this vol., i, 499), it should be possible to reduce a double linking in the side-chain of an aromatic acid in this way. This is confirmed by experiments with cinnamic acid. Sodium cinnamate is reduced in presence of nickel oxide at 300° to  $\beta$ -cyclohexylpropionic acid, whilst in presence of cupric oxide,  $\beta$ -phenylpropionic acid is obtained quantitatively. With copper as the catalyst, the reaction is incomplete, the product being a mixture of cinnamic and  $\beta$ -phenylpropionic acids.

The naphthoic acids require a higher temperature than benzoic acid.  $\beta$ -Naphthoic acid at 360° yields chiefly tetrahydro- $\beta$ -naphthoic acid with nickel oxide as catalyst. When the reaction is repeated, a mixture of decahydro- $\beta$ -naphthoic acid and decahydronaphthalene is obtained.  $\alpha$ -Naphthoic acid yields tetrahydronaphthalene.

C. H. D.

**Action of Iodine on Silver Benzoate and Salicylate.** NIKOLAI N. BUNGE (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 455—460).—It has been shown by Simonini (Abstr., 1893, i, 391) that at temperatures below 70° the interaction of iodine and the silver salt of a fatty acid gives rise to a compound of the anhydride of the acid with silver hypoiodite, thus:  $2R \cdot CO_2Ag + I_2 = AgI + (R \cdot CO)_2O, AgIO$ .

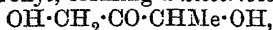
The author finds that silver benzoate and iodine yield a similar compound,  $Bz_2O, AgIO$ , which was isolated in an almost pure condition. This compound is only formed in entire absence of water, which decomposes it into benzoic acid and silver iodide and iodate. On heating, it decomposes rapidly, with evolution of carbon dioxide and organic products, silver iodide with a small admixture of silver being found in the residue.

With silver salicylate, no such compound was obtainable.

T. H. P.

**Dimethylketol. II. Conversion into a Ketotriose.** OTTO DIELS and ERICH STEPHAN (*Ber.*, 1909, 42, 1787—1792. Compare Abstr., 1907, i, 1000).—The benzoyl derivative of dimethylketol can be brominated without difficulty so as to introduce one or two atoms of bromine; both these enter the same methyl

group, forming the compounds (1)  $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{O}\cdot\text{COPh}$  and (2)  $\text{CHBr}_2\cdot\text{CO}\cdot\text{CHMe}\cdot\text{O}\cdot\text{COPh}$ . When cautiously hydrolysed with ice-cold dilute alkali, the benzoyl group is eliminated and the bromine atoms replaced by hydroxyl, forming a *ketotriose*,



and an *osone*,  $\text{CHO}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OH}$ . Both these yield the same osazone, identical with that derived from methylglyceraldehyde (compare Wohl and Franck, Abstr., 1902, i, 532). This behaviour establishes the above formula for the dibromide.

*Bromobenzoyldimethylketol*, prepared by bromination in chloroform solution in sunlight, crystallises in well formed, colourless prisms, m. p. 72–73°, and has a pleasant aromatic odour.

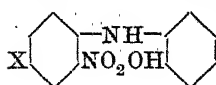
*Dibromobenzoyldimethylketol*, prepared by bromination with excess of bromine in chloroform solution and warming, forms similar crystals to the monobromo-derivative, and has m. p. 49°.

*Dihydroxymethylacetone* is obtained as a clear, yellow syrup, which showed signs of crystallising after a time. It tastes, like other methylated sugars, both bitter and sweet, reduces Fehling's solution in the cold, and reacts with phenylhydrazine, forming the osazone,  $\text{OH}\cdot\text{CHMe}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$ , m. p. 174°, to a yellow liquid crystallising in especially regularly formed, quadrate, golden crystals. The *acetylbenzoyl* derivative of dihydroxymethylacetone,  $\text{OBz}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OAc}$ , is obtained by the interaction of bromobenzoyldimethylketol with potassium acetate; it forms stellar aggregates of colourless, pointed needles, m. p. 54.5°.

E. F. A.

**Aromatic Compounds with Labile Halogen.** FRITZ ULLMANN (*Annalen*, 1909, 366, 79–118).—Investigation of the compounds derived from picryl chloride by replacing a nitro-group by a carboxyl, benzoyl, or sulphonyl group shows that the mobility of the chlorine atom is not hindered by the introduction of these groups.

It is also found that substituted dinitrohydroxydiphenylamines, like trinitrohydroxydiphenylamine (compare Turpin, Trans., 1891, 59, 72), give rise to derivatives of phenoxazine only, however, when the position 6 is occupied by a substituent; for example, compounds of



the annexed type, where  $\text{X} = \text{NO}_2$ ,  $\text{HSO}_3$ , or  $\text{CO}_2\text{H}$ , are not converted into phenoxazine derivatives when acted on by alkalis, although 2:6-dinitro-6'-hydroxydiphenylamine, when similarly treated, yields 5-nitrophenoxazine.

Derivatives of phenothiazine may be prepared in the manner originally employed by Kehrmann (Abstr., 1900, i, 61).

The formation of an azine could only be realised in one case, namely, the preparation of 4-aminophenazine by the reduction of 2:4-dinitro-6'-aminodiphenylamine-6-carboxylic acid.

[With GrADIENT ENGL.]—I. 2-Chloro-3:5-dinitrobenzoic Acid.—3:5-Dinitro-2-methylaminobenzoic acid,  $\text{C}_8\text{H}_7\text{O}_6\text{N}_3$ , prepared by the action of methylamine on 2-chloro-3:5-dinitrobenzoic acid, crystallises in orange-yellow needles, m. p. 233°. 3:5-Dinitro-2-dimethylamino-

benzoic acid,  $C_9H_9O_6N_3$ , obtained by similar means, crystallises in long, orange-yellow, prismatic needles, m. p.  $185^\circ$ . The chlorodinitrobenzoic acid, when heated with aniline in alcohol, yields the aniline salt of 2:4-dinitrodiphenylamine-6-carboxylic acid,  $C_{19}H_{15}O_6N_4$ , crystallising in red needles, m. p.  $192^\circ$ ; it readily passes into the yellow modification. 4-Nitro-2-aminodiphenylamine-6-carboxylic acid,  $C_{13}H_{11}O_4N_3$ , prepared by reducing the corresponding 2:4-dinitro-compound with the calculated quantity of ammonium sulphide, crystallises in glistening, reddish-brown needles, m. p.  $221^\circ$ . It is converted by sodium nitrite and acetic acid into 4-nitrophenaziminobenzene-6-carboxylic acid,  $C_{13}H_9O_4N_4$ , m. p.  $273^\circ$ .

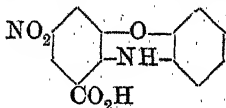
2:4-Diaminodiphenylamine-6-carboxylic acid,  $C_{13}H_{13}O_2N_3$ , obtained by reducing the dinitro-compound with excess of ammonium sulphide, forms glistening, yellowish-brown crystals, m. p.  $237-238^\circ$  (decomp.).

3:5-Dinitro-2-methoxybenzoic acid,  $\begin{array}{c} C(NO_2) \cdot CH : C \cdot CO_2H \\ | \\ CH \cdot C(NO_2) : C \cdot OMe \end{array}$ , prepared by the action of sodium methoxide in methyl alcohol on the chlorodinitrobenzoic acid, crystallises in white, glistening needles, m. p.  $165^\circ$ . The corresponding ethyl compound,  $C_9H_8O_5N_2$ , prepared in a similar manner, has m. p.  $133^\circ$ . 3:5-Dinitro-2-phenoxybenzoic acid,

$C_{13}H_8O_7N_2$ , prepared by heating the chlorodinitrobenzoic acid with sodium phenoxide at  $140-165^\circ$ , forms colourless crystals, m. p.  $150^\circ$ . It is converted by the action of phosphorus pentachloride in benzene into the chloride, which, when treated with aluminium chloride, yields 2:4-dinitroxanthone,  $C_6H_4 \begin{array}{c} \diagup CO \diagdown \\ \diagdown O \diagup \end{array} C_6H_2(NO_2)_2$ , crystallising in pale yellow needles, m. p.  $206^\circ$ .

Methyl 4:6:4':6'-tetranitrodiphenyl-2:2'-dicarboxylate,  $C_{16}H_{10}O_{12}N_4$ , prepared by treating methyl 2-chloro-3:5-dinitrobenzoate with copper at  $115-140^\circ$ , crystallises in almost colourless needles, m. p.  $176^\circ$ ; the acid,  $C_{14}H_6O_{12}N_4$ , crystallises in colourless needles, m. p. about  $284^\circ$  (decomp.).

2:4-Dinitro-2'-hydroxydiphenylamine-6-carboxylic acid,  $C_{13}H_9O_7N_3$ , obtained by the condensation of 2-chloro-3:5-dinitrobenzoic acid with o-aminophenol in the presence of sodium acetate, crystallises in glistening, reddish-brown needles, m. p.  $213^\circ$ . When warmed with aqueous sodium hydroxide, it yields 3-nitrophenoxazine-5-carboxylic acid (annexed formula), crystallising in orange-red needles, m. p.  $295^\circ$  (decomp.); the sodium salt,  $C_{13}H_7O_5N_2Na$ , forms brownish-red needles; the ammonium salt crystallises in glistening, bright red needles.



2:4-Dinitro-2'-aminodiphenylamine-6-carboxylic acid,  $C_{13}H_{10}O_6N_4$ , obtained by the condensation of 2-chloro-3:5-dinitrobenzoic acid with o-phenylenediamine, crystallises in red needles, and is converted by stannous chloride and hydrochloric acid into 4-aminophenazine, m. p.  $290-291^\circ$ ; Fischer gives m. p.  $274^\circ$  (Abstr., 1896, i, 628).

[With NICOLAS WOSNESSENSKY.]—II. 4-Chloro-3:5-dinitrobenzoic

*Acid.*—The following compounds were obtained by methods similar to those employed in the preparation of the isomeric 2-chloro-compounds.

Methyl 4-chloro-3:5-dinitrobenzoate has m. p. 105° and not 175° as given by Ullmann and Bielecke (Abstr., 1901, i, 586); the *ethyl* ester,  $C_9H_7O_6N_2Cl$ , has m. p. 83°.

3:5-Dinitro-4-methylaminobenzoic acid,  $C_8H_7O_6N_3$ , crystallises in yellow needles, m. p. 218°. The corresponding dimethylamino-compound,  $C_9H_9O_6N_3$ , forms orange-yellow needles, m. p. 246°. 2:6-Dinitro-2'-hydroxydiphenylamine-4-carboxylic acid,  $C_{18}H_{13}O_7N_3$ , crystallises in red needles with a metallic lustre, m. p. 216°; it is converted by aqueous sodium hydroxide into 5-nitrophenoxazine-3-carboxylic acid,  $C_{13}H_8O_5N_2$ , crystallising in violet needles.

4-Chloro-3:5-dinitrobenzoic acid condenses with *o*-aminothiophenol, yielding 2:6-dinitro-2'-thio-oxydiphenylamine-4-carboxylic acid, which crystallises in yellow needles, m. p. 254°, and is converted by a dilute solution of sodium hydroxide into 5-nitrophenothiazine-3-carboxylic acid,

$C_6H_4 \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} C_6H_2(NO_2)_2 \cdot CO_2H$ , dark violet, felted needles, m. p. about 316°; the sodium salt forms violet crystals.

4-Chloro-3:5-dinitrobenzophenone,  $C_{13}H_7O_5N_2Cl$ , prepared by treating a solution of 4-chloro-3:5-dinitrobenzoic acid in benzene with phosphorus pentachloride and subsequently with aluminium chloride, crystallises in yellow rhombohedra, m. p. 118°; it is converted (1) by an aqueous alcoholic solution of sodium hydroxide into 3:5-dinitro-4-hydroxybenzophenone,  $C_{13}H_8O_6N_2$ , almost colourless needles, m. p. 136°; (2) by aqueous ammonia into 3:5-dinitro-4-aminobenzophenone,  $C_{13}H_9O_5N_3$ , long, pale-yellow needles, m. p. 148°; (3) by aniline in alcohol into 2:6-dinitro-4-benzoyldiphenylamine,  $C_{19}H_{13}O_5N_3$ , orange-yellow needles, m. p. 211°; (4) by condensation with *o*-aminophenol into 2:6-dinitro-2'-hydroxy-4-benzoyldiphenylamine,  $C_{19}H_{13}O_6N_3$ , brick-red crystals, m. p. 220° (decomp.), which is converted by dilute aqueous sodium hydroxide into 5-nitro-3-benzoylphenoxazine,

$C_{19}H_{12}O_4N_2$ , glistening, red leaflets, m. p. 216°; (5) by condensation with *o*-aminothiophenol into 2:6-dinitro-4-benzoyl-1-anilino-2'-thiophenol,  $C_{19}H_{13}O_5N_3S$ , yellow crystals, m. p. 200° (decomp.), which, when treated with dilute alcoholic sodium hydroxide, yields 5-nitro-3-benzoylphenothiazine,  $C_{19}H_{12}O_5N_2S$ , reddish-violet needles, m. p. 200° (decomp.).

[With EMIL KUHN.]—III. 4-Chloro-3:5-dinitrobenzenesulphonic Acid. —Potassium 4-chloro-3:5-dinitrobenzenesulphonate,  $C_6H_2O_7N_2S_2ClK$ , crystallises in white, glistening scales, m. p. 293°; the sulphonyl chloride,  $C_6H_2O_6N_2SO_2Cl$ , forms colourless prisms, m. p. 89°, and is converted by aniline into 2:6-dinitrodiphenylamine-4-sulphonanilide,  $C_{18}H_{14}O_6N_3S$ , red, felted needles, m. p. 200°. The latter substance is converted by hot dilute aqueous sodium hydroxide into 2:6-dinitrophenol-4-sulphonanilide,  $C_{13}H_9O_7N_2S$ , crystallising in leaflets with a bronzy reflex, m. p. 177°. The potassium salt above mentioned is converted by dilute aqueous ammonia into potassium 2:6-dinitroaniline-4-sulphonate,  $C_6H_4O_7N_3SK$ , thin, yellow leaflets, which explode slightly when heated. Potassium 4-chloro-3:5-dinitrobenzenesulphonate reacts with aniline,

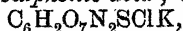
yielding *aniline 2:6-dinitrodiphenylamine-4-sulphonate*,  $C_{18}H_{16}O_7N_4S$ , which crystallises in large, orange-yellow needles, m. p.  $252^\circ$  (decomp.).

*Potassium 5-nitrophenoxazine-3-sulphonate*,  $C_{12}H_7O_6N_2SK$ , crystallises in brownish-red needles with a bronzy lustre; it is converted by aniline into the *aniline salt*,  $C_{18}H_{16}O_6N_3S$ , red needles with a metallic lustre, m. p.  $285^\circ$  (decomp.).

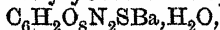
*Potassium 5-nitrophenothiazine-3-sulphonate*,  $C_{12}H_7O_5N_2S_2K$ , forms coppery-red crystals.

*2:6-Dinitro-2-hydroxydiphenylamine*,  $C_{12}H_9O_5N_3$ , crystallises in fan-shaped groups of long, reddish-violet needles, m. p.  $191^\circ$ ; it is converted by a 1% aqueous solution of sodium hydroxide into *5-nitrophenoxazine*,  $C_{12}H_8O_3N_2$ , crystallising in violet needles, m. p.  $166^\circ$ .

[With ERICH HERRE.]—IV. *2-Chloro-3:5-dinitrobenzenesulphonic Acid*.—*2-Chloro-5-nitrobenzenesulphonic acid* is converted by a mixture of concentrated nitric acid and fuming sulphuric acid (23%  $SO_3$ ) into *2-chloro-3:5-dinitrobenzenesulphonic acid*; the *potassium salt*,



crystallises in glistening, white leaflets or needles. The latter substance is converted (1) by ammonia into *potassium 2:4-dinitroaniline-6-sulphonate*,  $C_6H_4O_7N_2SK$ , crystallising in yellow prisms, which explode slightly when heated; (2) by potassium hydroxide into *potassium 2:4-dinitrophenol-6-sulphonate*,  $C_6H_3O_8N_2SK$ , pale yellow needles, which explode slightly when heated; the *dipotassium salt*,  $C_6H_3O_8N_2SK_2$ , forms intensely yellow needles; the *barium salt*,



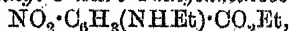
is a yellow, crystalline powder; (3) by aniline into *aniline 2:4-dinitrodiphenylamine-6-sulphonate*,  $C_{18}H_{16}O_7N_4S$ , glistening, yellow needles.

*Sodium 3-nitrophenoxazine-5-sulphonate*,  $C_{12}H_7O_6N_2SNa$ , crystallises in reddish-brown, glistening needles, and is reduced by zinc dust and ammonium chloride, yielding *3-aminophenoxazine-5-sulphonic acid*,  $C_{12}H_{10}O_4N_2S$ , which crystallises in almost colourless, long, slender needles.

*Sodium 3-nitrophenothiazine-5-sulphonate*,  $C_{12}H_7O_5N_2S_2Na$ , crystallises in glistening, brownish-violet needles. W. H. G.

**Nitration of *p*-Diethylaminobenzoic Acid.** FRÉDÉRIC REVERDIN and A. DE LUC (*Ber.*, 1909, 42, 1725—1730. Compare Abstr., 1906, i, 273; 1907, i, 620; 1908, i, 167).—*3-Nitro-4-ethylaminobenzoic acid* (Baudisch, Abstr., 1907, i, 132) is the chief product obtained by adding *p*-diethylaminobenzoic acid to nitric acid (30%) at  $10^\circ$ , and then allowing the temperature to rise to  $25$ — $30^\circ$ . The same product is formed at different temperatures, and also when working in acetic acid solution. Other products formed at the same time are 1:3-dinitro-diethylaniline (van Romburgh, *Rec. trav. chim.*, 1883, 2, 40, 104, 107), 1:3-dinitroethylaniline, and 1:3:5-trinitroethylaniline. In only one experiment was mononitroethylaniline isolated.

Ethyl *p*-diethylaminobenzoate (Folin, *Amer. Chem. J.*, 1887, 9, 331) when nitrated yields *ethyl 3-nitro-4-ethylaminobenzoate*,



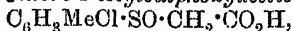
which crystallises in lemon-yellow needles, m. p.  $92^\circ$ . When the nitra-

tion is carried out in acetic acid solution, *ethyl 3:5-dinitro-4-ethylnitrosoaminobenzoate*,  $\text{NO} \cdot \text{NEt} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2\text{Et}$ , lemon-yellow plates, m. p.  $72^\circ$ , and trinitroethylaniline are also formed. When oxidised with nitric acid (D 152) the nitrosoamine yields the corresponding *nitroamine*,  $\text{NO}_2 \cdot \text{NEt} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2\text{Et}$ , which crystallises in colourless, pearly plates, m. p.  $96^\circ$ . With alcoholic potassium hydroxide, it gives a reddish-violet coloration. When boiled with dilute nitric acid, the nitrosoamine yields *3:5-dinitro-4-ethylaminobenzoic acid*.

The ester of the nitroamino-acid when boiled with sodium carbonate solution yields *3:5-dinitro-4-ethylnitroaminobenzoic acid*, which crystallises in pale yellow plates, m. p.  $181^\circ$ .

When the 3-nitro-4-ethylaminobenzoic acid is nitrated in acetic acid solution at  $45^\circ$  with fuming nitric acid, the products are *3:5-dinitro-4-ethylnitrosoaminobenzoic acid*,  $\text{NO} \cdot \text{NEt} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2\text{H}$ , yellow plates, m. p.  $152^\circ$ , *3:5-dinitro-4-ethylaminobenzoic acid*, and *2:4-dinitroethylaniline*.  
J. J. S.

[Preparation of Arylsulphoxyacetic Acids.] KALLE & Co. (D.R.-P. 208343).—*p-Chloro-o-tolylsulphoxyacetic acid*,

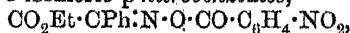


white needles, is obtained by oxidising *p-chloro-o-tolylthiolacetic acid*,  $\text{C}_6\text{H}_3\text{MeCl} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , with alkaline hypochlorite. The homologues are similarly prepared. When any of these arylsulphoxyacetic acids containing a free ortho-position are treated with chlorosulphonic acid they give rise to vat dyes.  
F. M. G. M.

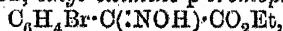
**Condensation of Alkyl Nitrates or Nitrites with Ethyl Phenylacetate.** WILHELM WISLICENUS and RUDOLF GRÜTZNER (*Ber.*, 1909, 42, 1930—1940. Compare Abstr., 1902, i, 541).—Ethyl nitrate or nitrite does not condense with ethyl acetate, laevulate, or succinate, but successful results have been obtained with a few compounds containing the groups  $\cdot\text{CH}_2\text{Ph}$  or  $\cdot\text{CH}_2\text{CN}$ .

When equal molecular quantities of ethyl nitrate and ethyl phenylacetate, or *ethyl p-bromophenylacetate*, m. p.  $30^\circ$ , b. p.  $142\text{—}144^\circ/12\text{—}14\text{ mm.}$ , are introduced into a cold alcoholic-etheral solution of potassium ethoxide (1 mol.), the potassium salt of phenylnitromethane or *p-bromo-o-nitrotoluene* and ethyl carbonate are formed.

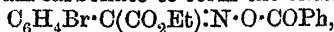
The interaction of equal molecular quantities of ethyl nitrite, ethyl phenylacetate, and potassium ethoxide in cold ethereal solutions yields the yellow, crystalline *potassium* salt of ethyl oximinophenylacetate,  $\text{CO}_2\text{Et} \cdot \text{CPh} \cdot \text{N} \cdot \text{OK}$ , the cold aqueous solution of which, by acidification, yields Gabriel's ethyl oximinophenylacetate, which is freed from the simultaneously-formed oximinophenylacetic acid (detected by the red coloration with ferric chloride) by removing the latter as the copper salt by distillation in a vacuum or by crystallisation from benzene and light petroleum. The potassium salt reacts with *p*-nitrobenzoyl chloride to form two isomeric *p-nitrobenzoates*,



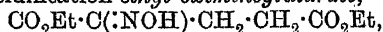
m. p.  $112\text{—}113^\circ$  and  $137\text{—}138^\circ$  respectively. By the interaction of ethyl nitrite, ethyl *p*-bromophenylacetate, and potassium ethoxide and subsequent acidification, *ethyl oximino-p-bromophenylacetate*,



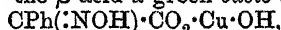
m. p. 159°, is obtained in colourless needles, which reacts with benzoyl chloride and potassium carbonate to form the *benzoate*,



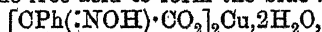
m. p. 90—91°. A benzene solution of succinonitrile and amyl nitrite (2 mols.) reacts with cold alcoholic-etheral potassium ethoxide to form a brown *potassium salt*, from which by acidification *αβ-dioximino-succinonitrile*,  $\text{CN}\cdot\text{C}(\text{:NOH})\cdot\text{C}(\text{:NOH})\cdot\text{CN}$ , m. p. 137—138° (decomp.), is obtained, which separates from water in colourless leaflets containing  $3\text{H}_2\text{O}$  and melting at 86° to a green liquid. Ethyl nitrite, potassium ethoxide, and ethyl  $\alpha$ -acetoglutarate react in cold alcoholic-etheral solution to form, by elimination of ethyl acetate, a *potassium salt*, which yields by acidification *ethyl oximinoglutarate*,



m. p. 62—63°, which is also obtained from nitrosylsulphuric acid and ethyl  $\alpha$ -acetoglutarate in concentrated sulphuric acid, and on hydrolysis yields Wolff's  $\alpha$ -oximinoglutaric acid. The copper salts of the  $\alpha$ - and the  $\beta$ -forms of oximinophenylacetic acid, described by Hantzsch, are basic salts; a solution of copper acetate or sulphate precipitates from an ethereal solution of the  $\beta$ -acid a green *basic copper salt*,



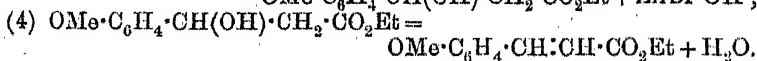
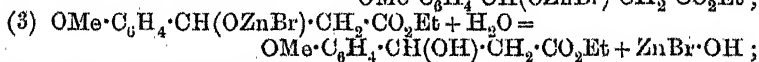
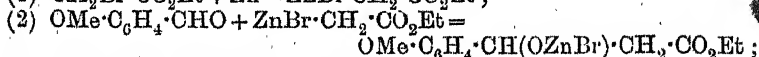
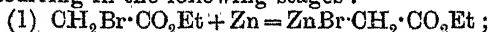
which reacts with the free acid to form the blue *normal salt*,



which is violet when anhydrous.

C. S.

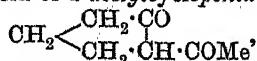
**Synthesis of Methoxycinnamic Acid.** NIKOLAI N. BUNGE (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 460—463).—The action of zinc on a mixture of ethyl bromoacetate and anisaldehyde (compare Andriewsky, Abstr., 1908, i, 799) gives rise to ethyl methoxycinnamate (compare Vorländer, Abstr., 1897, i, 272), the reaction occurring in the following stages:



T. H. P.

**Ring Formation in Ketonic Acids.** EDMOND É. BLAISE and A. KOEHLER (*Compt. rend.*, 1909, 148, 1401—1404. Compare this vol., i, 204).—The authors give an account of the conversion of the esters of  $\epsilon$ - and  $\delta$ -ketonic acids into cyclic compounds.

On treating the ethyl ester of heptan- $\epsilon$ -onoic acid with sodium ethoxide an excellent yield of 1-acetylcyclopentan-2-one,



is obtained. This has b. p. 75°/8 mm. and shows the reactions of a  $\beta$ -diketone. On ethylation it yields 1-acetyl-1-ethylcyclopentan-2-one,  $\text{C}_9\text{H}_{15}\text{O}_2$ , b. p. 97—99°/15 mm.; sodium ethoxide converts this into the ethyl ester of  $\delta$ -ethylheptan- $\epsilon$ -onoic acid,  $\text{COMe}\cdot\text{CHEt}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{Et}$ ,

b. p. 134—136°/14 mm. 1-Propionylcyclopentan-2-one,  $C_8H_{12}O_2$ , prepared from the ethyl ester of octan-ε-onoic acid, has b. p. 90°/13 mm. The methyl and ethyl derivatives of this diketone have also been prepared.

Propionylcyclohexanone,  $CH_2 \begin{smallmatrix} CH_2-CO \\ CH_2 \cdot CH_2 \end{smallmatrix} CH \cdot COEt$ , b. p. 122—123°/21 mm., is prepared from the ethyl ester of octan-ζ-onoic acid. Owing to the ease with which the ring is opened, alkylation of the acetyl-cyclohexanones leads to the formation of a mixture of the alkylacetyl-cyclohexanone with the original ketonic ester.

The authors have not succeeded in preparing cyclic compounds from η-ketonic esters. W. O. W.

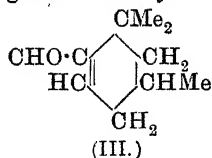
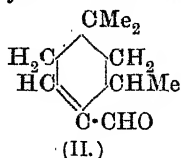
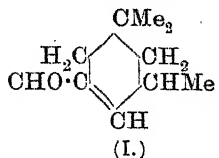
Reduction of αβ-Unsaturated Ketones and Aldehydes. ALADAR SKITA (*Ber.*, 1909, 42, 1627—1636).—Usually αβ-unsaturated alicyclic ketones when treated with mild reducing agents give bimolecular ketones; with stronger agents the ketonic group is reduced as well as the ethenoid linking, and in a number of instances further complications ensue. It has been found that reduction of the ethenoid linking takes place readily without these complications when the substance in alcoholic solution is mixed with an aqueous solution of palladium chloride and gum arabic and the resultant solution exposed to hydrogen gas. *iso*Phorone is transformed into dihydroisophorone in 82% yield in two hours; ethyl 1-methyl-Δ<sup>1</sup>-cyclohexene-3-one-6-carboxylate gives a 94% yield of the ethyl 1-methyl-cyclohexane-3-one-6-carboxylate, the oxime hydrochloride of which was analysed. Ethyl 1:3-dimethyl-Δ<sup>3</sup>-cyclohexenone-5-carboxylate gave ethyl 1:3-dimethylcyclohexanone-5-carboxylate,  $C_{11}H_{18}O_3$ , b. p. 133—135°/12 mm.; the oxime,  $C_{11}H_{19}O_2N$ , is an oil. Ethyl *isophorone*-carboxylate on reduction gave both modifications of ethyl dihydroisophoronecarboxylate (*Abstr.*, 1907, i, 1041), and phorone itself gave diisobutylcarbinol (*Grignard*, *Abstr.*, 1901, i, 679).

The aliphatic αβ-unsaturated aldehyde citral gave by Sabatier's method a series of cyclic compounds (*Enklaar*, *Abstr.*, 1908, i, 664), but palladium gives quite different results; 2 atoms of hydrogen are absorbed, and citronellal and citronellol are obtained together with an oil, b. p. 139—140°/15 mm., m. p. 57°. It is a bimolecular aldehyde, probably  $OMe_2CH \cdot [CH_2]_2 \cdot CHMe \cdot CH \cdot CHO$  β-cycloCitral gave 2:2:6-trimethylhexahydrobenzaldehyde on reduction. W. R.

Synthesis of Violet Perfumes. I. GEORG MERLING and ROBERT WELDE [in part, HEINRICH EICHWEDE and ALADAR SKITA] (*Annalen*, 1909, 366, 119—216).—An account of the authors' work on the synthesis of violet perfumes, the experimental part of which treats, however, only of the preparation and properties of some of the intermediate compounds obtained in the synthesis of α- and β-irone (compare *Tiemann*, *Abstr.*, 1894, i, 80; 1898, i, 376).

With the object of obtaining information on the relationship existing between the constitution of a substance and its odour, the following aldehydes were prepared (compare *Abstr.*, 1903, i, 502, 764; 1905, i, 653)

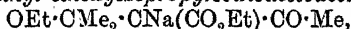
and their condensation products with acetone examined. As a result, it is found that the aldehydes derived from *cyclogeraniolenes* yield



products with acetone having an odour of violets when the aldehyde group is situated next to a methyl group or dimethyl group or between these groups; in the latter case the odour is exceedingly intense. The character of the acetone condensation product as a perfume disappears when the aldehyde group does not adjoin a methyl group.

The grouping  $-\text{CMe}_2 \cdot \text{C}(\text{CHO}) \cdot \text{CMe}-$  does not lead to the production of violet perfumes unless present in the *cyclogeraniolene* ring; for example, the condensation product of  $\beta$ -isopropylbutaldehyde with acetone does not smell like violets.

I. *Ethyl isoPropylideneacetoacetate*.—This ester combines with sodium ethoxide, yielding *ethyl ethoxyisopropylsodioacetoacetate*,



obtained as colourless, felted needles. It is a very unstable substance, being converted by carbon dioxide in aqueous solution into *ethyl ethoxyisopropylacetoacetate*, part ( $\frac{1}{3}$ ) of which decomposes, yielding ethyl dimethylacrylate and ethyl acetate, whilst the remainder yields ethyl *isopropylideneacetoacetate* and alcohol. The sodium compound, when treated with methyl iodide in the absence of alcohol, yields ethyl trimethylacrylate, and, when acted on by an alcoholic solution of ethyl iodide, yields ethyl ether, ethyl acetate, ethyl dimethylacrylate (90%), ethyl *isopropylideneacetoacetate*, and an oil, b. p. above  $93^\circ/7$  mm.

II. *Ethyl isoPhoroncarboxylate*.—An account of the preparation and properties of this compound has appeared previously (Abstr., 1905, i, 349). Contrary to the view advanced by Rabe (Abstr., 1906, i, 89), it is shown that this ester exists in a ketonic and enolic form. The pure *keto*-modification is a colourless oil, b. p.  $135-142^\circ/10.5-12$  mm.; the *enol*-form could not be isolated in a pure state. Ethyl *isophoronecarboxylate* is converted by sodium ethoxide and ethyl iodide into *ethyl isophoronecarboxylate ethyl ether*,  $\begin{array}{c} \text{CH} \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\ | \\ \text{C}(\text{OEt}) \cdot \text{CH} \cdot \text{CMe}_2 \end{array}$ , a colourless oil, b. p.  $136-137^\circ/8$  mm. An ethyl group is undoubtedly attached to oxygen in this compound, since it is hydrolysed by barium hydroxide solution, yielding *isophorone*.

III. *Reduction of Ethyl isoPhoroncarboxylate*.—The reduction of ethyl *isophoronecarboxylate* with sodium and alcohol leads to the production of a mixture of four stereoisomeric ethyl 4-hydroxycyclogeraniolancarboxylates and the corresponding hydroxy-carbinols, the esters of two stereoisomeric hydroxy-acids, isomeric with 4-hydroxycyclogeraniolancarboxylic acid, but probably containing a five-membered ring system, and small quantities of other substances.

A *hydroxycarbinol*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ | \\ \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHMe} \end{array}$ , was isolated in a state of purity from the mixture obtained in the manner just described.

it crystallises in glistening prisms, m. p. 92—93°, b. p. 152°/8 mm.; the *diacetyl* derivative,  $C_{14}H_{24}O_4$ , is a colourless, odourless, viscid oil, b. p. 148—153°/10 mm.; the *oxalyl* derivative,  $C_{12}H_{18}O_4$ , is a colourless, crystalline powder, m. p. 248°.

IV. *Stereoisomeric 4-Hydroxycyclogeraniolane-carboxylic Acids* (2 : 6 : 6-Trimethyl-4-cyclohexanol-carboxylic Acids).—*cis*-4-Hydroxy- $\alpha$ -cyclogeraniolane-carboxylic acid,  $C_{10}H_{18}O_2$ , crystallises in large, thin, iridescent scales, m. p. 145°; it changes into the *trans*-modification when kept, and, when distilled in a vacuum, is largely converted into the *trans*-form, yielding at the same time a small quantity of the lactone. The *ethyl* ester cannot be obtained in a pure state, since it partly breaks down into lactone and alcohol when distilled in a vacuum; the ester obtained after distillation is a colourless, viscid oil, b. p. 140—147°/11 mm. The *acetyl* derivative,  $C_{12}H_{20}O_4$ , crystallises in glistening prisms, m. p. 121—122°, and is converted by thionyl chloride into the *chloride*,  $C_{12}H_{19}O_3Cl$ , a colourless, limpid oil, b. p. 129—131°/8 mm. The *lactone*,  $C_{10}H_{16}O_2$ , crystallises in glistening, thick plates, m. p. 57·5—58°, b. p. 114·5°/6 mm., 119·5°/7 mm.

*trans*-4-Hydroxy- $\alpha$ -cyclogeraniolane-carboxylic acid crystallises in glistening prisms, m. p. 154—155°, b. p. 189—190°/7·5 mm.; it is converted into the *cis*-isomeride, and subsequently into the lactone, when distilled with potassium hydrogen sulphate at 116—134°/8·5 mm. and when boiled with 30—40% sulphuric acid. It yields the *acetyl* derivative just described when treated with acetic anhydride and a drop of concentrated sulphuric acid. The *ethyl* ester,  $C_{12}H_{22}O_3$ , is obtained as a silky, crystalline mass, b. p. 136·5°/7 mm., 134°/6 mm., 139°/8 mm.

*Ethyl 4-chloro-2 : 6 : 6-trimethylcyclohexane-1-carboxylate*,  $C_{12}H_{21}O_2Cl$ , obtained by the action of phosphorus pentachloride on the ester just described, is a colourless, odourless, limpid oil, b. p. 111—112°/6·5 mm.; the corresponding *bromo*-derivative,  $C_{12}H_{21}O_2Br$ , has b. p. 125—128°/6 mm.

*cis*-4-Hydroxy- $\beta$ -cyclogeraniolane-carboxylic acid forms small, glistening crystals, m. p. 157—158°, b. p. 179·5°/7 mm. It decomposes at 240° into water and *lactone*,  $C_{10}H_{16}O_2$ , obtained as small, glistening crystals, m. p. 37—39°, b. p. 121·5°/5 mm., 127°/7 mm., 129°/8 mm., 134°/5·5 mm. The *acetyl* derivative,  $C_{12}H_{20}O_4$ , crystallises in glistening prisms, m. p. 143—144°. The *ethyl* ester,  $C_{12}H_{22}O_3$ , is a colourless, odourless, viscid oil, b. p. 136·5°/5 mm.

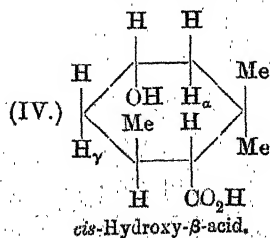
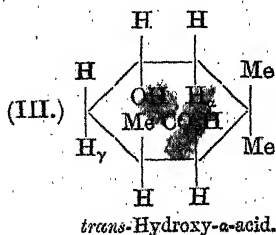
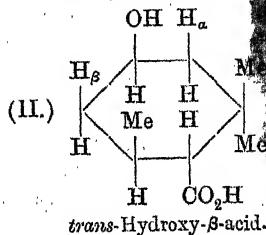
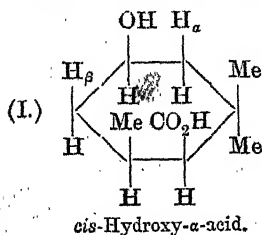
*trans*-4-Hydroxy- $\beta$ -cyclogeraniolane-carboxylic acid forms small, colourless crystals, m. p. 151—152°, b. p. 176—177°/5 mm. It decomposes slowly at 300°, yielding the lactone, m. p. 37—39°, and is partly converted by heating for four hours with 40% sulphuric acid into the *cis*-form, which passes into  $\Delta^3$ -cyclogeranic acid. The *acetyl* derivative,  $C_{12}H_{20}O_4$ , crystallises in rosettes of colourless prisms, m. p. 110—111°. The *ethyl* ester is a colourless, viscid oil, b. p. 124°/5 mm. It is possible to convert *cis*-4-hydroxy- $\alpha$ -cyclogeraniolane-carboxylic acid into *trans*-4-hydroxy- $\beta$ -cyclogeraniolane-carboxylic acid by the following series of changes. The *acetyl* derivative of the former compound is acted on by phosphorus pentachloride, and the *chloride* so formed decomposed by water. The *acetylated* acid thus obtained, when hydrolysed with alcoholic potassium hydroxide, yields the *trans*- $\beta$ -compound.

*Ethyl 4-keto- $\alpha$ -cyclogeraniolane-carboxylate*,  $C_{12}H_{20}O_3$ , obtained by oxidising the corresponding *cis*- or *trans*-hydroxy- $\alpha$ -compound, is a colourless, crystalline mass, and has b. p.  $124^\circ/7$  mm.,  $119^\circ/6$  mm.; the *oxime*,  $C_{12}H_{21}O_3N$ , crystallises in glistening prisms, b. p.  $148$ — $156^\circ/6$  mm.; it does not melt at a constant temperature ( $99$ — $117^\circ$ ); when reduced with sodium and alcohol it yields ethyl 4-amino-2:6:6-trimethylcyclohexanecarboxylate (compare Skita, Abstr., 1907, i, 1040), b. p.  $114$ — $115^\circ/6$  mm. The latter substance when treated successively with methyl iodide and methyl-alcoholic potassium hydroxide yields the *iodide*,  $C_{15}H_{30}O_2NI$ ; the corresponding *hydroxide* decomposes to a slight extent at  $235^\circ$  into trimethylamine and ethyl  $\Delta^2$ -cyclogeranate, but chiefly into methyl alcohol and ethyl 4-dimethylamino-2:6:6-trimethylcyclohexane-1-carboxylate,  $C_{14}H_{27}O_2N$ , a colourless oil b. p.  $115$ — $116^\circ/6$  mm. *Ethyl 4-keto- $\beta$ -cyclogeraniolane-carboxylate* is a colourless, viscid oil, b. p.  $130^\circ/7$  mm. The *oxime*, obtained in the same manner as the  $\alpha$ -compound, crystallises in glistening prisms and needles, m. p.  $89$ — $90^\circ$ .

4-Keto- $\alpha$ -cyclogeraniolane-carboxylic acid,  $C_{10}H_{16}O_3$ , cannot be prepared by hydrolysing the ester. It is obtained by oxidising the 4-hydroxy- $\alpha$ -acid, and crystallises in glistening prisms, m. p.  $127$ — $128^\circ$ , b. p.  $174$ — $175^\circ/7$  mm. 4-Keto- $\beta$ -cyclogeraniolane-carboxylic acid, prepared in a similar manner, forms glistening prisms, m. p.  $118$ — $120^\circ$ , b. p.  $174$ — $175^\circ/7$  mm.

The esters of the above keto-acids condense with benzaldehyde in the presence of sodium ethoxide, yielding chiefly the *monobenzylidene* derivative,  $C_{12}H_{18}O_2 \cdot CHPh$ , a pale yellow oil, b. p.  $200$ — $202^\circ/5$  mm., whilst a mixture of mono- and di-benzylidene derivatives is obtained when hydrogen chloride is the condensing agent. The *dibenzylidene* compound could not be obtained in a pure condition.

V. *Configurations of the Stereoisomeric 4-Hydroxycyclogeraniolane-carboxylic Acids*.—This part of the paper is devoted to the deduction of the space formulæ of the 4-hydroxy-2:6:6-trimethylcyclohexane-1-carboxylic acids.—The following formulæ are assigned to the four acids:



In agreement with these formulæ are the following facts: (1) The acids (I) and (III) yield the same keto-acid when oxidised; the same also applies to the acids (II) and (IV). (2) The esters of the  $\beta$ -acids (II) and (IV) are hydrolysed with greater ease than the corresponding  $\alpha$ -compounds, probably because of the steric hindrance produced by the two adjacent methyl groups in the latter case. (3) Water is eliminated from the acids (I) and (II) with exceedingly great difficulty, and only then after rearrangement into the other forms. On the contrary, water is eliminated from the acids (III) and (IV) with great readiness. In these two acids, the hydrogen atom ( $H_\gamma$ ), which is in the same plane as the hydroxyl group with which it combines, is not influenced by a neighbouring methyl group as in the acids (I) and (II) ( $H_\beta$ ). (4) Elimination of water from all four acids leads to the formation of the two stereoisomeric modifications of  $\Delta^3$ -cyclogeranic acid. A  $\Delta^4$ -cyclogeranic acid is not produced, owing to the hindering influence of the adjacent methyl group on the hydrogen atom  $H_\alpha$ .

V.I. *Stereoisomeric Methylisopropyl-3-cyclopentanolicarboxylic Acids* (?).—It is probable that the esters of these two acids present to the extent of 10% in the product obtained by reducing ethyl isophoroncarboxylate are stereoisomeric *ethyl 5-methyl-1-isopropyl-3-cyclopentanolicarboxylates*,  $\text{CH}_3 \begin{matrix} \text{CH(OH) \cdot CH}_2 \\ \text{CHMe} - \text{CPr}_\beta - \text{CO}_2\text{Et} \end{matrix}$  but confirmation of this is lacking. They are therefore designated provisionally *cis*-hydroxy-acid C and *trans*-hydroxy-acid C.

*cis*-Hydroxy-acid C,  $\text{C}_{10}\text{H}_{18}\text{O}_3$ , crystallises in glistening prisms or slender needles, m. p.  $137-138^\circ$ ; it dissociates into water and lactone at  $1-2^\circ$  above its m. p., also when boiled for a short time with 10% sulphuric acid. The *ethyl* ester is a colourless, viscid oil, which at  $103.5-114^\circ/6$  mm. breaks down completely into alcohol and lactone. The *lactone*,  $\text{C}_{10}\text{H}_{16}\text{O}_2$ , forms large, glistening, brittle crystals, m. p.  $43-44^\circ$ , b. p.  $112-113^\circ/7$  mm.,  $246^\circ/760$  mm.

*trans*-Hydroxy-acid C,  $\text{C}_{10}\text{H}_{18}\text{O}_3$ , crystallises in large, glistening prisms, m. p.  $185-186^\circ$ , b. p.  $192^\circ/8$  mm. It passes at  $270-280^\circ$  into the *cis*-form, which at once breaks down into water and lactone; the *ethyl* ester,  $\text{C}_{12}\text{H}_{22}\text{O}_3$ , is a colourless, viscid oil, b. p.  $129.5^\circ/6$  mm.

Either of the esters just described when oxidised yields the *ethyl* ester of the *keto*-acid,  $\text{C}_{12}\text{H}_{20}\text{O}_3$ , a colourless, odourless, viscid oil, b. p.  $123^\circ/7$  mm.; the *oxime* crystallises in colourless, crystalline nodules, m. p.  $118-120^\circ$ . The *acid*,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , crystallises in rosettes of needles, m. p.  $123-124^\circ$ ; the *barium* salt forms flat, spear-shaped crystals; the *dibenzylidene* derivative,  $\text{C}_{26}\text{H}_{28}\text{O}_3$ , crystallises in slender, yellow needles, m. p.  $112-114^\circ$ .

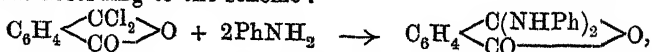
W. H. G.

**Amine Salts of Phthalamic, Phenylphthalamic, and Phenylsuccinamic Acids.** SHIGERU KOMATSU (*Mem. Coll. Sci. Eng. Kyōto*, 1908, 1, 431-436).—Aniline *o*-sulphanilino benzoate has been obtained by Remsen and Kohler (*Abstr.*, 1895, i, 473), and aniline benzanilinosulphonate and toluidine benzanilinosulphonate by Sohn (*Abstr.*, 1898, i, 428); but hitherto no amine salts of phenylphthalamic acid have not been obtained. The author has succeeded in preparing these by mixing absolute alcoholic solutions of amine and acid, and leaving the mixture for some days. *Aniline phenylphthamate*,

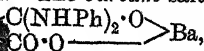
$\text{NHPH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{NH}_2\text{Ph}$ , forms white, hexagonal crystals, m. p. 124—125°, which are decomposed by alkali or acid, or on heating in alcoholic or aqueous solution, into aniline and phenylphthalimide; the *methylamine* salt, colourless needles, m. p. 115°; the  *$\beta$ -naphthylamine* salt, a white, crystalline precipitate, m. p. 170—173°, and the *benzylamine* salt, colourless needles, m. p. 138—139°, behave similarly. *Methylamine phthalamate* consists of colourless needles, m. p. 146—148°; *aniline phthalamate*,  $\text{CONH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{NH}_2\text{Ph}$ , has m. p. 185—187°.

*Methylamine phenylsuccinamate*,  $\text{CONHPh} \cdot \text{C}_2\text{H}_4 \cdot \text{CO}_2 \cdot \text{NH}_2\text{Me}$ , forms colourless needles, m. p. 115—120°. E. H.

**Isomeric Phenylphthalimides and Some Allied Compounds.** MITSURU KUHARA and SHIGERU KOMATSU (*Mem. Coll. Sci. Eng. Kyoto*, 1908, 1, 391—405).—By the action of aniline on phthalyl chloride, Fukui and Kuhara (*Abstr.*, 1902, i, 34) obtained an *as*-phenylphthalimide. Hoogewerff and van Dorp (*Abstr.*, 1903, i, 174), and also Dunlap and Cummer (*Abstr.*, 1903, i, 699), failed, however, to obtain the latter compound, and the former authors claim that the product of the reaction is a mixture of phthalanilide and *N*-phenylphthalimide, and that van der Meulen's phthalophenylisoimide (*Abstr.*, 1897, i, 281) is really *as*-phenylphthalimide. The present authors, repeating Kuhara and Fukui's experiments, have failed to isolate the substance described by them. When solutions of phthalyl chloride (1 mol.) and aniline (4 mols.) in 95% alcohol, each cooled at  $-10^\circ$ , are mixed, phthalanilide is precipitated. The filtrate, after a time, deposits *N*-phenylphthalimide and a white, crystalline precipitate of *as*-dianilinophthalic acid,  $\text{C}_{20}\text{H}_{18}\text{O}_3\text{N}_2$ , m. p. 175—176°. Although the latter compound, which behaves as a dibasic acid, has the composition corresponding with hydrated phthalanilide, it is never formed from phthalanilide by the action of water. It seems probable that it is formed by the hydration of the lactonic *as*-phthalanilide, which could be formed from *as*-phthalyl chloride according to the scheme:

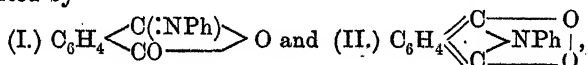


and hence would have the constitution  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NHPH})_2 \cdot \text{OH}$ . This view is supported by the fact that when heated in dry chloroform with phosphorus pentachloride, it gives a mixture of *N*-phenylphthalimide and von Gerichten's phthalanil,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{NPh}) \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{NPh}$  (*Abstr.*, 1880, 473), which is also obtained when *N*-phthalanilide is treated with the same dehydrating agent (compare Remsen, *Abstr.*, 1897, i, 244; Henderson, *Abstr.*, 1901, i, 208). *as*-Dianilinophthalic acid is an unstable substance, decomposing into aniline and *N*-phenylphthalimide when treated with hot alcohol, acetic acid, or alkali, or on heating alone at  $100^\circ$ . It is split up by hot hydrochloric acid into aniline, *N*-phenylphthalimide, and phthalic acid. The barium salt,



forms a slightly yellow crystalline precipitate; the silver salt,  $\text{CO}_2\text{Ag} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NHPH})_2 \cdot \text{OAg}$ , a white, crystalline precipitate. The authors made repeated attempts to obtain van der Meulen's phthalophenylisoimide, but without success. When phenylphthalamic acid is

treated with acetyl chloride, a pale yellow substance is produced, having a variable m. p. (93—125°). From this, colourless needles, m. p. 83—84°, of a substance,  $C_{14}H_9O_2N$ , can be isolated, which is isomeric, but not identical, with either *n*-phenylphthalimide or Kuhara and Fukui's *as*-phenylphthalimide. To it the authors assign the name *β-as-phenylphthalimide*. The pale yellow substance on recrystallisation also gives amber-coloured, rhombic prisms, m. p. 125—126°, of a second *isomeride* of phenylphthalimide, also different from the *as*-phenylphthalimide and phthalophenylisomide. *β-as*-Phenylphthalimide in ethereal solution readily changes into *N*-phenylphthalimide. The latter is formed, together with aniline and phthalic acid, when the amber-coloured isomeride in acetic acid solution is heated at 120°. The possible formulæ of isomeric phenylphthalimides can be represented by



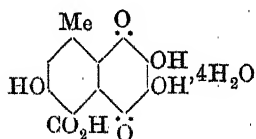
of which (I) can exist in two stereoisomeric forms. Owing to its colour and the fact that (like phthalylperoxide) crystals of it gently detonate on sudden heating, the second formula is suggested for the amber-coloured isomeride. The *β-as*-phenylphthalimide is supposed to have one of the two stereoisomeric forms, and either Kuhara and Fukui or van der Meulen's compound, the other. Possibly, however, van der Meulen's phthalophenylisomide is the pale yellow compound described above, that is, a mixture of two isomerides, particularly as this author gives the m. p. 115—116°, whilst Hoogewerff and van Dorp give 120—122°.

E. H.

**Synthesis of Ethyl *p*-Orsellate.** ANDREAS LIPP and E. SCHELLER (*Ber.*, 1909, 42, 1967—1972. Compare this vol., i, 451).—In the preparation of hexan-ε-one-β-ol, alcoholic ethyl sodioacetoacetate and propylene bromide are heated in a sealed vessel on the water-bath, the alcohol is removed by distillation, the residue is washed with water, and the insoluble oil is repeatedly shaken with dilute potassium hydroxide. The combined aqueous and alkaline washings when acidified with sulphuric acid deposit after some weeks a substance which is proved to be ethyl *p*-orsellate (Senhofer and Brunner, *Abstr.*, 1881, 265) by its conversion, by boiling 10% potassium hydroxide and subsequent acidification, into orcinol (*dibenzoate*,  $C_6H_5Me(O \cdot COPh)_2$ , m. p. 86—87°).

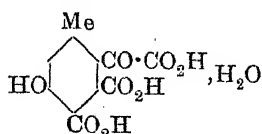
C. S.

**Carminic Acid.** OTTO DIMROTH (*Ber.*, 1909, 42, 1611—1627, 1735).—This communication deals largely with a re-investigation of the oxidation products of carminic acid with a view to establish its constitution. When an aqueous solution of this acid at 0° is treated with sulphuric acid and potassium permanganate, 7—8 equivalents of oxygen are used up in oxidising it. This solution on standing for three-quarters of an hour at 90° evolves carbon dioxide, and the ether extract gives *carminazarin*, annexed



formula, which crystallises from water in garnet-red needles, decomp.

240—250°. The *potassium* salt,  $C_{13}H_7O_7K$ , is violet. It is very similar to *isonaphthazarin* in its behaviour; its alkaline solution turns quickly to



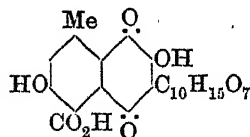
5:6-dicarboxy-4-hydroxy-o-tolyl glyoxylic acid, annexed formula, when a stream of oxygen is passed through the solution at 70°; it crystallises in colourless needles, m. p. 230° (decomp.); phenylhydrazine gives the phenylhydrazine salt of the *phenylhydrazone*,

$C_{23}H_{22}O_7N_4$ , which forms almost colourless leaflets. When heated with sulphuric acid, this dicarboxylic acid forms cochinelic acid and carbon dioxide.

Another similarity to *isonaphthazarin* is the behaviour of *carminazarin* towards nitric acid in glacial acetic acid, the tetraquinone, *carminazarinquinone*, annexed formula, being obtained; this forms almost colourless prisms, and when heated with water or acetic acid passes back into *carminazarin*. The aqueous solution is turned first yellowish-brown by alkalis, then green, and finally blue.

The intermediate compound formed in the oxidation of *carminic* acid by permanganate at 0° is best observed when the barium salt is used; an almost colourless barium salt is finally obtained, which yields an almost colourless acid,  $C:O:H = 1:0.94:1.75$ . It is believed to be of the nature of a  $\alpha$ -hydroxy- $\alpha$ -carboxylic acid, which would therefore readily pass into the *carminazarin*.

*Carminic* acid when oxidised in acetic acid with manganese dioxide gives *carminoquinone*, which has not been isolated, but regenerates the parent acid on reduction with sulphur dioxide.



*Carminic* acid is considered not to be a symmetrical compound, but to have the annexed constitution, the nature of the  $C_{10}H_{15}O_7$  group remaining to be determined. W. R.

**Alkylated Carminic Acids.** CARL LIEBERMANN and HANS LIEBERMANN (*Ber.*, 1909, 42, 1922—1930).—A paper published in consequence of Dimroth's recent reference to dimethylcarminic acid (preceding abstract).

*Carminic* acid, which is not esterified by alcoholic hydrogen chloride, yields with methyl sulphate and 10% potassium hydroxide only a red, crystalline *dimethoxy*-derivative,  $C_{22}H_{20}O_{11}(OMe)_2$ ; the acid and silver oxide moistened with ether form with methyl iodide a mixture of the *pentamethoxy*- and the *hexamethoxy*-derivatives,  $C_{22}H_{17}O_8(OMe)_5$  and  $C_{22}H_{16}O_7(OMe)_6$ , which have respectively an orange and a yellow colour, and are separated by the solubility of the former in 1% sodium hydroxide.

Dealkylation of the preceding ethers by concentrated hydrochloric acid at 70° yields the *tetramethoxy*-compound,  $C_{22}H_{18}O_9(OMe)_4$ . The presence of the methoxyl in place of the hydroxyl groups has the usual effect of decreasing the solubility of the ethers in water, and

diminishes the colour intensity; the di- and tetra-methoxy-derivatives alone form lakes.

An almost complete dealkylation of the ethers is effected by hydrobromic acid, D 149, at 95–100°, the product being the anhydrocarminic acid, which is obtained by heating carminic acid alone at 150° (Abstr., 1898, i, 682), or with hydrobromic acid at 100°. By treatment with silver oxide and methyl iodide, anhydrocarminic acid yields a brownish-red *tetramethoxy*-derivative,  $C_{22}H_{12}O_6(OMe)_4$ , which is insoluble in alkalis.

One probable result of the oxidation of carminic acid to carminazarin (Dimroth, *loc. cit.*) will be the rejection of the bisindone formula of the former; this is not a necessary consequence, however, for even if carminazarin eventually proves to be a naphthalene derivative, its formation from an indone compound is not without analogy in the conversion of indones into naphthalene derivatives. The authors point out that the formula of carminic acid suggested by C. Liebermann and Voswinkel (Abstr., 1904, i, 903) receives support from the discovery of carminazarin; they are inclined to retain the indone formula for  $\alpha$ - and  $\beta$ -bromocarmin (Abstr., 1897, i, 539). C. S.

**Benzoylacrylic Acid. Condensation of Glyoxylic Acid with Certain Ketones.** J. BOUGAULT (*Compt. rend.*, 1909, 148, 1270–1272. Compare Abstr., 1908, i, 796; this vol., i, 102).—The fixation of acetophenone by benzoylacrylic acid, whereby diphenacylacetic acid is produced, is not due to direct combination, as previously supposed, but arises from the decomposition of benzoylacrylic acid into acetophenone and glyoxylic acid, followed by condensation of 2 mols. of the former with 1 mol. of the latter. This is supported by the observation that  $\alpha$ -hydroxy- $\beta$ -benzoylpropionic acid gives diphenacylacetic acid under the same conditions. This acid, moreover, is obtained in excellent yield by allowing a mixture of glyoxylic acid and acetophenone to remain for twenty-four hours in contact with dilute aqueous alkali containing a little alcohol.

The following compounds have been prepared in the same way: *dianisacylacetic acid*,  $CH(CH_2 \cdot CO \cdot C_6H_4 \cdot OMe)_2 \cdot CO_2H$ , m. p. 112°; *dipiperacylacetic acid*,  $CH(CH_2 \cdot CO \cdot C_4H_8 \cdot O_2 \cdot CH_2)_2 \cdot CO_2H$ , m. p. 112°. W. O. W.

**Organic Syntheses by means of Sunlight. III. Phenyl isoAmyl Ketone and Physical Constants of Compounds of Amylene with Benzaldehyde and Ketones.** EMANUALE PATERNO and F. TRAETTA-MOSCA (*Gazzetta*, 1909, 39, i, 449–454).—In order to throw light on the constitution of the compound yielded by benzaldehyde and amylenes ( $\beta$ -methyl- $\Delta^2$ -butylene) (this vol., i, 393), the authors have prepared phenyl isoamyl ketone from isoamyl iodide and benzonitrile by means of the Grignard reaction (compare Blaise, Abstr., 1902, i, 164). The ketone is a transparent liquid, b. p. 255–256°, with a faint aromatic odour, and on cooling solidifies to a white, crystalline mass, m. p. –2°, and is probably identical with the ketone, b. p. 240–241°/720 mm., obtained by Perkin and Calman (Trans., 1886, 49, 166). Its *semicarbazone*,  $C_5H_{11} \cdot CPh \cdot N \cdot NH \cdot CO \cdot NH_2$ , m. p.

150—151°, and *oxime*, m. p. 71—72°, were prepared, but it was not found possible to obtain the phenylhydrazone. The results show, however, that the compound obtained by Paternò and Chieffi (this vol., i, 323) cannot be regarded as a phenyl amyl ketone, since it does not give the characteristic ketone reactions.

The densities of this compound, and also of phenyl *iso*amyl ketone, have been determined at various temperatures with the following results. (1) Phenyl *iso*amyl ketone:  $D_4^0$  0.9744,  $D_4^{15}$  0.9623,  $D_4^{21.3}$  0.9498,  $D_4^{45.5}$  0.9363,  $D_4^{100}$  0.8925; the molecular volume is hence 180.74 at 0°, 183.0 at 15°, and 230.1 at 255°. (2) Compound obtained from benzaldehyde and amylene:  $D_4^0$  0.9855,  $D_4^{15.3}$  0.9731,  $D_4^{24.1}$  0.9583,  $D_4^{54.5}$  0.9413,  $D_4^{99.5}$  0.9047; molecular volume, 178.7 at 0°, 181.0 at 15°, and 220.5 at 231°. These numbers are in agreement with the general rule, that molecular volumes of ketones are greater than those of non-ketonic compounds.

The non-existence of a carbonyl oxygen in the compound obtained from benzaldehyde and amylene is also supported by the value of the index of refraction.

T. H. P.

**New Derivatives of Catechol.** I. LAZENNEC (*Bull. Soc. chim.*, 1909, [iv], 5, 501—509).—A continuation of the work of Moureu on catechol derivatives (Abstr., 1899, i, 433, 494, 679, 700). Bromoacetophenone,  $\text{COPh}\cdot\text{CH}_2\text{Br}$ , condenses with the sodium derivative of catechol in presence of alcohol to form *o*-hydroxyphenoxyacetophenone,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COPh}$ , m. p. 111°, which crystallises from benzene in colourless needles, is readily soluble in alcohol, ether, or chloroform, less so in benzene, and insoluble in water or light petroleum. The *oxime*, m. p. 109°, forms colourless needles from benzene or methyl alcohol; the *hydrazone*, m. p. 91°, separates from a mixture of benzene and light petroleum in small, bright yellow crystals; the *semicarbazone*, m. p. 145.5°, is colourless, and crystallises from methyl alcohol. The *benzoate*, m. p. 136—137°, forms colourless, rectangular tablets from methyl alcohol; the *methyl ether*, m. p. 101°, crystallises from ether in long, colourless needles, and the *ethyl ether*, m. p. 81°, forms somewhat truncated, rectangular tablets from alcohol.

On treatment with nitric acid ( $D$  1.42) in presence of acetic acid, *o*-hydroxyphenoxyacetophenone yields a dinitro-derivative, m. p. 168°, which crystallises from alcohol in golden-yellow needles. This is oxidised by permanganate to benzoic acid, and when boiled during four hours with hydrobromic acid furnishes Nietzki and Moll's 3:5-dinitrocatechol (Abstr., 1893, i, 699). From these results and analogy with the nitration of guaiacol (Grimaux and Lefèvre, Abstr., 1891, 1031), it is concluded that the dinitro-derivative has the nitro-groups in the catechol nucleus and occupying positions 3 and 5 with respect to the hydroxyl group.

T. A. H.

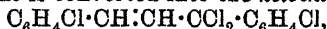
**Fission of Phenyl Aryl Ketones and Phenyl Naphthyl Ketones by Sodamide.** Mlle. PAULINE LUCAS (*Ann. Chim. Phys.*, 1909, [8], 17, 127—139. Compare Haller, Abstr., 1908, i, 987).—The constitution of the ketones obtained by treating *o*-, *m*-, and *p*-xylenes with benzoyl chloride in presence of aluminium chloride has been

determined by allowing the ketones to react with sodamide, and then examining the products of decomposition when the sodium derivative is treated with water. Thus the ketone obtained from *o*-xylene is shown to be phenyl *o*-xylyl ketone ( $\text{Me}_2\text{CO} = 1:2:4$ ), since the additive compound it forms with sodamide yields on hydrolysis a mixture of benzamide and the amide of 1:2:4-xylic acid. The action of benzoyl chloride on *m*-xylene leads to the formation of a non-homogeneous substance containing phenyl *m*-xylyl ketone ( $\text{Me}_2\text{CO} = 1:3:4$ ). The ketone obtained from *p*-xylene has been identified with phenyl *p*-xylyl ketone ( $\text{Me}_2\text{CO} = 1:4:5$ ).

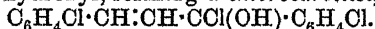
The reaction between phenyl  $\beta$ -naphthyl ketone and sodamide follows the usual course; in the case of phenyl  $\alpha$ -naphthyl ketone, however, the sodium compound,  $\text{C}_{10}\text{H}_7\text{-CPh(ONa)NH}_2$ , regenerates the ketone when treated with water and yields only traces of benzamide.

W. O. W.

Dibenzylideneacetone and Triphenylmethane. III. Ketochloride and Chlorocarinol of *p,p*-Dichlorobenzylideneacetophenone [*p*-Chlorophenyl *p*-Chlorostyryl Ketone]. FRITZ STRAUS and A. ACKERMANN (*Ber.*, 1909, 42, 1804—1823. Compare Straus and Caspari, *Abstr.*, 1907, i, 609; Straus and Ecker, *Abstr.*, 1906, i, 859).—*p*-Chlorophenyl *p*-chlorostyryl ketone is easily prepared by the condensation of *p*-chlorobenzaldehyde with *p*-chlorobenzophenone by Claisen's method. It is converted into the ketochloride,



on boiling with phosphorus pentachloride in benzene solution; this crystallises very well. It does not form an additive compound with bromine. In all instances the group  $\text{OCl}_2$  reacts, so that only one chlorine atom is replaced; thus moist silver oxide replaces one of the chlorine atoms by hydroxyl, forming a chlorocarinol,



The behaviour is thus completely analogous to that of dibenzylideneacetone [distyryl ketone]. In presence of hydrogen chloride in neutral solvents or acetyl chloride it is re-converted into the ketochloride.

When kept or even on boiling with methyl alcohol it could not be converted into the methyl ether, and to prepare this compound the presence of traces of mineral acids are necessary. The chlorocarinol can be heated for a short time above its melting point before a slow decomposition takes place. On prolonged heating, change takes place with the formation of ketone; the primary change consists in the elimination of water to form anhydrides, which could not be isolated. At higher temperatures, a second decomposition sets in, which gives rise to ketochloride, and by reactions brings about the decomposition of this; this phase is particularly marked if the heating is not carried out in a vacuum so as to remove the water formed in the primary change. The chlorocarinol is completely stable towards reagents which eliminate hydrogen chloride, for example, silver salts, alkalis, and tertiary bases.

Ketochloride, carbinol, and methyl ether all dissolve in concentrated sulphuric acid with an intense, yellowish-red coloration, due to the

formation of the same sulphate in each case. The ketochloride and carbinol dissolve in liquid sulphur dioxide without colour, due to their dissociation being very small. The corresponding *chlorobromide*,  $C_6H_4Cl \cdot CH : CH \cdot CClBr \cdot C_6H_4Cl$ , also forms colourless, concentrated solutions in sulphur dioxide, but these gain rapidly in colour when diluted.

*p*-Chlorophenyl *p*-chlorostyryl ketone crystallises in well-formed, yellow plates, m. p. 156—157°, and dissolves in concentrated sulphuric acid with an intense yellow colour and a strong, green fluorescence. The introduction of the two para-chlorine atoms causes the colour as compared with phenyl styryl ketone to be distinctly more red. The *dibromide*,  $C_6H_4Cl \cdot CHBr \cdot CHBr \cdot CO \cdot C_6H_4Cl$ , forms snow-white, soft needles, m. p. 160—161°. The *phenylhydrazone* separates in colourless, matted needles, m. p. 149°. Its solutions show an intense, bright blue fluorescence.

The *ketochloride*, that is, *p*-chlorophenyl-*p*-chlorostyryldichloromethane,  $C_6H_4Cl \cdot CH : CH \cdot CCl_2 \cdot C_6H_4Cl$ , crystallises in colourless, transparent prisms, m. p. 54—55°. It dissolves in concentrated sulphuric acid to a reddish-yellow liquid, and does not form an additive compound with bromine or a coloured complex with mercuric chloride; with tin tetrachloride a deep violet precipitate is obtained; this is strongly dissociated in solution.

The *methyl ether* of the chlorocarbinol,  
 $C_6H_4Cl \cdot CH : CH \cdot CCl(OMe) \cdot C_6H_4Cl$ ,  
 is obtained as a bright yellow oil.

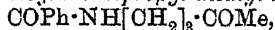
Acetic acid acts on the ketochloride, forming the compound  
 $OAc \cdot CCl(CH : CHPh)_2$   
 and eliminating hydrogen chloride. A state of equilibrium is rapidly reached, and subsequently the amount of acid liberated slowly increases. The ketochloride of *pp*-dichlorostyryl ketone behaves similarly, but the hydrolysis of the ketone commences only after prolonged action.

*pp*-Dichlorophenylstyrylchlorocarbinol,  
 $C_6H_4Cl \cdot CH : CH \cdot CCl(OH) \cdot C_6H_4Cl$ ,  
 forms colourless, matted needles, m. p. 67—68°. E. F. A.

Dibenzylideneacetone and Triphenylmethane. IV. Differences in the Reactivity of Halogens in the  $-CCl_2$ -Group. FRITZ STRAUS and WERNER HÜSSY (*Ber.*, 1909, 42, 2168—2182).—The authors have studied the rate at which the halogen in the  $-CCl_2$ -group is replaced by hydroxyl by shaking ethereal solutions of various compounds with water, and titrating the amount of free hydrochloric acid contained in 20 c.c. of the aqueous layer by means of *N*/10-alkali hydroxide; the results are illustrated by means of curves. A certain parallelism seems to exist between the reactivity of the halogens and their electrolytic dissociation; since the latter phenomenon is accompanied by the formation of coloured ions, the authors examined the absorption spectra of phenyl styryl ketone and distyryl ketone and several of their derivatives in sulphuric acid solution. The bearing of the experimental results on the transformation of the ordinary valency into Werner's carbonium valency is discussed. P. H.

**New Methods of Preparation of Aliphatic Amino-ketones.** SIEGMUND GABRIEL (*Ber.*, 1909, 42, 1238—1243. Compare also following abstracts).—Phthalylglycyl chloride and its homologues easily exchange chlorine for phenyl, and yield phthalimino-derivatives of aliphatic aromatic ketones,  $C_8H_4O_2 \cdot N \cdot [CH_2]_x \cdot C(Ph)$ , and from these by hydrolysis the mixed amino-ketones are obtained (compare Abstr., 1908, i, 649). Two methods for preparing aliphatic amino-ketones have been devised: (1) Phthalylglycyl chloride by condensation, for example, with ethyl sodiomalonate gives either ethyl phthalylglycyl-malonate or ethyl phenylglycylacetate by the loss of the carboxy-group. Hydrolysis of the acetate gives phthaliminoacetone, and afterwards  $\alpha$ -aminoacetone. (2) The other method consists in condensing a bromoalkylphthalimide with ethyl sodioacetoacetate and hydrolysis of the resulting ethyl phthaliminoalkylacetoacetate, which yields finally an aminoalkyl ketone or its anhydride, carbon dioxide being liberated.

When bromoethylphthalimide is boiled with an alcoholic solution of ethyl sodioacetate for four to five hours and the oily product hydrolysed with 20% hydrochloric acid, 2-methylpyrroline (Hielscher, Abstr., 1898, i, 338) is obtained. The platinichloride has m. p. 200° (decomp.), and the aurichloride, m. p. 154—157° (decomp.). This on benzoylation gives  *$\gamma$ -benzoylaminoethyl methyl ketone*,



which crystallises from ether in needles, m. p. 66—67°.

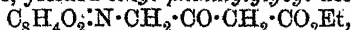
In a similar manner  *$\gamma$ -bromopropylphthalimide* yields 2-methyl-tetrahydropyridine (compare Lipp, Abstr., 1896, i, 317) in addition to  *$\delta$ -phthaliminobutyl methyl ketone*, which was only obtained in an impure condition. The intermediate product, *ethyl phthaliminopropyl-acetoacetate*,  $C_8H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} N \cdot [CH_2]_3 \cdot CH(COMe) \cdot CO_2Et$ , has also been

isolated; it separates from ether in snow-white crystals, m. p. 65°.

W. R.

**Phthaliminoacyl Chlorides and Ethyl Sodiomalonate.** SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1909, 42, 1243—1249. Compare preceding abstract).—Condensation of ethyl sodiomalonate with phthaliminoacyl chlorides is not possible in alcoholic solution, as the acyl chloride forms an ester. The general method employed was to prepare the ethyl sodiomalonate by dissolving the finely divided metal in a benzene solution of ethyl malonate. To the gelatinous mass so obtained the phthaliminoacyl chloride in benzene was added, and after twelve hours the liquid was heated at 100°. The excess of sodium was then removed by hydrochloric acid, the benzene and unchanged ester distilled in a current of steam, and from the oily residues left behind the various derivatives were prepared.

The oil from the interaction of phthalylglycyl chloride and ethyl sodiomalonate gave, on treatment with hydrogen iodide (b. p. 127°), *phthaliminoacetone*,  $C_8H_4O_2 \cdot N \cdot CH_2 \cdot COMe$ , m. p. 124°. The oil, when rubbed with alcohol, yielded *ethyl phthalylglycyl acetate*,



which crystallises from alcohol in needles, m. p. 110°.

The oil from  *$\beta$ -phthalylalanine chloride* and ethyl sodiomalonate

crystallises slowly, and on recrystallisation from methyl alcohol *ethyl β-phthalylalanylacetate*,  $C_8H_4O_2 \cdot N \cdot [CH_2]_2 \cdot CO \cdot CH_2 \cdot CO_2Et$ , is obtained in slender prisms, m. p. 121—122°. When the crude substance is boiled for four hours with 20% hydrochloric acid, *methyl β-amino-propyl ketone* was obtained. It was characterised by its *platinichloride*,  $C_8H_{20}O_2N_2Cl_6Pt$ , which forms yellow plates, 195—205° (decomp.)—the *picrate* is yellow, m. p. 129—130°—and *aurichloride*, m. p. 152° (decomp.).

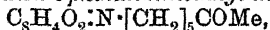
On the other hand, the oil from  $\gamma$ -phthaliminobutryl chloride yields, on hydrolysis with 20% hydrochloric acid, 2-methylpyrroline.  $\delta$ -Phthaliminovaleryl chloride on similar treatment gives 2-methyltetrahydropyridine in 35% yield. These two ring compounds are best prepared from the bromoalkylphthalimides (compare preceding abstract).

W. R.

**$\epsilon$ -Amino-ketones.** SIEGMUND GABRIEL (*Ber.*, 1909, 42, 1249—1259. Compare Abstr., 1908, i, 648).— $\epsilon$ -Aminohexophenone is stable and does not form an anhydro-derivative, unlike the  $\gamma$ - and  $\delta$ -aminoketones. It has been considered desirable to study a purely aliphatic  $\epsilon$ -amino ketone from this point of view.

A new and more convenient method for the preparation of  $\epsilon$ -aminohexophenone is through  $\epsilon$ -benzoyl leucine ( $\epsilon$ -benzoylaminohexoic acid). This acid (compare Braun, this vol., i, 230) is obtained from  $\epsilon$ -chloro-amylobenzamide by converting into nitrile and hydrolysis of the nitrile. The acid has been characterised by its *silver* salt,  $C_{13}H_{16}O_3NaAg$ . The  $\epsilon$ -benzoylaminohexoyl chloride was next prepared, and this on heating with aluminium chloride in benzene forms  $\epsilon$ -benzoylaminohexophenone,  $COPh \cdot NH \cdot [CH_2]_5 \cdot COPh$ , which separates from alcohol in crystals, m. p. 95°. When this ketone is heated with glacial acetic and hydrochloric acids at 170° for three hours,  $\epsilon$ -aminohexophenone hydrochloride is formed. The *picrate*,  $C_{18}H_{20}O_8N_4$ , crystallises from water with 1 mol.  $H_2O$ , m. p. 95°, and from alcohol in anhydrous condition, m. p. 128—129°.

A better method of preparing  $\delta$ -bromobutylphthalimide (Abstr., 1899, i, 595) from  $\gamma$ -chlorobutyronitrile is described. This imide, on boiling for five hours with sodium ethoxide and ethyl acetoacetate, yields the corresponding phthalimino-ester, which gives on hydrolysis with 20% hydrochloric acid  $\epsilon$ -phthaliminoamyl methyl ketone,



in largest amount; it crystallises in snow-white leaflets, m. p. 71—72°; a quantity of methyl  $\epsilon$ -aminoamyl ketone is formed at the same time. For this preparation it is much better to use  $\delta$ -iodobutylphthalimide,  $C_{12}H_{12}O_2NI$ , and potassium ethoxide. The iodo-derivative is obtained by heating  $\delta$ -phenoxybutylphthalimide and hydriodic acid for one and a-quarter hours, and forms needles, m. p. 88—89.5°; some  $\delta$ -iodobutylamine hydriodide is formed simultaneously. When  $\epsilon$ -phthaliminoamyl methyl ketone is heated with a mixture of hydrochloric and glacial acetic acids for three hours in a sealed tube at 170°, *methyl  $\epsilon$ -aminoamyl ketone*,  $NH_2 \cdot [CH_2]_5 \cdot COMe$ , is formed; the *platinichloride*,  $C_{14}H_{22}O_2N_2Cl_6Pt$ , forms orange leaflets, m. p. 180—181° (decomp.); the *picrate*,  $C_{13}H_{20}O_9N_4 \cdot H_2O$ , needles, m. p. 79—80°. It

has been found better, however, when preparing larger quantities of the compound to condense  $\epsilon$ -benzoylaminoheptoyl chloride and ethyl sodiomalonate in benzene solution and hydrolyse the resulting ester with hydrochloric acid.

When methyl  $\epsilon$ -aminoamyl ketone picrate is heated at  $100^\circ$  it loses 2 mols. of water and forms the *picrate* of cyclo-2-methyldehydrohexamethyleneimine,  $\text{MeC} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$ ,  $\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , which crystallises

from alcohol in needles, m. p.  $188-189^\circ$ . The anhydro-heptacyclic base has not been obtained from the  $\epsilon$ -amino-ketone hydrochloride and 33% potassium hydroxide; the oily base so obtained gives with phenylthiocarbimide, *phenylacetylamiylthiocarbamide*,  $\text{COMe} \cdot [\text{CH}_2]_5 \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ ,

which crystallises from alcohol in prisms, m. p.  $99.5^\circ$ . That the hydrochloric acid solution contains the  $\epsilon$ -amino-ketone is shown by its yielding the *phenylhydrazone*,  $\text{N}_2\text{HPh} \cdot \text{COMe} \cdot [\text{CH}_2]_5 \cdot \text{NH}_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , which crystallises from acetone in leaflets, m. p.  $98-99^\circ$  (decomp.), and gradually decomposes in the air. The oily base when treated with solid potassium hydroxide gave an oil, b. p.  $60-160^\circ/19$  mm. The fraction b. p.  $100-160^\circ/19$  mm. gave, on analysis, numbers intermediate between those of the amino-ketone and anhydro-base, both fractions gave the same picrate as previously obtained.

The ease with which the anhydro-base picrate passes back into the amino-ketone picrate is noteworthy; a solution of the anhydro-base picrate in 50% alcohol on evaporation in the air deposits the picrate of the ketone. This formation of an unstable heptacyclic base distinguishes methyl  $\epsilon$ -aminoamyl ketone from the phenyl  $\epsilon$ -aminoamyl ketone.

W. R.

**Reduction of  $\epsilon$ -Amino-ketones.** SIEGMUND GABRIEL (*Ber.*, 1909, 42, 1259-1268).—The easy formation of an unsaturated seven-membered ring compound, 2-methylcyclodehydrohexamethyleneimine (preceding abstract), suggested experiments being carried out to reduce this to 2-methylhexamethyleneimine, a reaction which proceeds easily with five- and six-membered *cycloimines* (*Abstr.*, 1908, i, 275, 649). As the *cycloimine* had not been obtained pure, methyl  $\epsilon$ -aminoamyl ketone hydrochloride was reduced with sodium and alcohol and the product distilled in a current of steam; 2-methylcyclo-

hexamethyleneimine,  $\text{NH} \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$ , is an oil, b. p.  $148-150^\circ/760$  mm.,  $D_{20}^{20}$  0.8590,  $n_D^{20}$  1.45862, having a powerful coniine-like odour and a strong alkaline reaction; the *hydrochloride*,  $\text{C}_7\text{H}_{16}\text{NCl}$ , forms silken needles, m. p.  $196^\circ$ ; the *aurichloride*,  $\text{C}_7\text{H}_{16}\text{NCl}_4\text{Au}$ , golden-yellow needles, m. p.  $95^\circ$ ; the *platinichloride*, needles, m. p.  $196^\circ$ ; the *picrate*, m. p.  $131^\circ$ ; the *nitrosoamine*,  $\text{C}_7\text{H}_{14}\text{ON}_2$ , is a yellow oil, b. p.  $240-242^\circ/746$  mm.; the *benzenesulphonyl* derivative forms crystals, m. p.  $78^\circ$ .

This easy formation of a seven-membered ring is somewhat surprising, although the lactam of  $\epsilon$ -aminohexanoic acid is formed to a slight extent from the acid (*Abstr.*, 1899, i, 595). Blaise and

Houillon (Abstr., 1906, i, 692, 704) have shown that *cyclooctamethyleneimine* is not obtained from octamethylenediamine hydrochloride by heat, but 2-butylpyrrolidine, and that instead of *cyclodecamethyleneimine*, 2-hexylpyrrolidine is the product when a similar experiment is carried out. As the tendency in these imines, as in other cases, is to form five- or six-membered rings, it was necessary to ascertain if, in the compound under consideration, 2-propylpyrrolidine was not the substance really obtained: 2-ethylpiperidine is already known and differs from it.

2-Propylpyrrolidine,  $\text{NH} \begin{array}{c} \text{CHPr} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{array}$ , was therefore synthesised

by two different methods, and shown to be different from the imine prepared by the reduction of the  $\epsilon$ -amino-ketone. The first method used was to condense ethyl sodioethylmalonate with  $\gamma$ -phthalimino-butyryl chloride in dry benzene, hydrolyse the ethyl phthalimino-butyrylethylmalonate with hydrochloric acid to 2-propylpyrrolidine, reduce this with tin and hydrochloric acid to 2-propylpyrrolidine, isolate the benzenesulphonyl derivative, and hydrolyse this with a mixture of glacial acetic and hydrochloric acids in a sealed tube at  $170^\circ$  for one and a-half hours. The yield by this method was very meagre, and the second method was accordingly devised, namely, to condense bromoethylphthalimide and ethyl potassiobutyrylacetate in benzene; subsequent hydrolysis of the ester gives 2-propylpyrrolidine, which was worked up as in the first method. The *hydrochloride* is deliquescent; the *platnichloride* has m. p.  $92^\circ$  when it contains water of crystallisation, and  $135^\circ$  when anhydrous; *aurichloride*, m. p.  $120^\circ$ , and the *picrate*, m. p.  $104-104.5^\circ$ ; 1-benzenesulphonyl-2-propylpyrrolidine,  $\text{C}_{18}\text{H}_{19}\text{O}_2\text{NS}$ , crystallises from alcohol in needles, m. p.  $66-67.5^\circ$ .

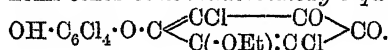
$\epsilon$ -Aminohexophenone on reduction with sodium and alcohol gives 2-phenylcyclohexamethyleneimine,  $\text{C}_{12}\text{H}_{17}\text{N}$ , a basic, colourless oil, b. p.  $276-278/753$  mm.; its *hydrochloride*,  $\text{C}_{12}\text{H}_{18}\text{NCl}$ , m. p.  $205-206^\circ$ ; *aurichloride*,  $\text{C}_{12}\text{H}_{18}\text{NCl}_4\text{Au}$ , needles, m. p.  $166^\circ$ ; *platnichloride*,  $\text{C}_{24}\text{H}_{36}\text{N}_2\text{Cl}_6\text{Pt}$ , orange, hexagonal plates, m. p.  $197^\circ$  (decomp.); *picrate*, yellow prisms, m. p.  $154^\circ$ . It also yields an oily *nitrosoamine*, and 1-benzenesulphonyl-2-phenylhexamethyleneimine,  $\text{C}_{18}\text{H}_{21}\text{O}_2\text{NS}$ , plates, m. p.  $81-82^\circ$ .

W. R.

Benzoquinone from the Standpoint of the Law of Entropy and the Partial Valency Hypothesis. ARTHUR MICHAEL (*J. pr. Chem.*, 1909, [ii], 79, 418-440).—A theoretical paper in which the characteristic chemical behaviour of benzoquinone is explained by reference to the chemical potential and the entropy relationships of its various transformations. It is likewise shown that the arguments based on the partial valency hypothesis employed by Thiele (Abstr., 1899, i, 554) and Posner (Abstr., 1904, i, 1029) to account for the chemical changes of benzoquinone are quite untenable.

W. H. G.

**Hemi-Ether of Hexachloroethoxy-*o*-quinocatechol.** C. LORING JACKSON and G. L. KELLEY (*Ber.*, 1909, 42, 1865—1867).—The product obtained by the action of ethyl alcohol on tetrachloro-*o*-benzoquinone, and melting at 210° (decomp.) (*Abstr.*, 1907, i, 856), appears to be the hemi-ether of *hexachloroethoxy-*o*-quinocatechol*,



The same product is formed by the action of ethyl alcohol on hexachloro-*o*-quinocatechol ether or on the half ether of heptachloro-*o*-quinocatechol. When reduced with an alcoholic solution of sulphur dioxide, it yields a compound,  $\text{C}_{14}\text{H}_8\text{O}_5\text{Cl}_6$ , m. p. 173°, from which a *tetra-acetyl* derivative,  $\text{C}_{14}\text{H}_8\text{Ac}_4\text{O}_5\text{Cl}_6$ , m. p. 165°, is obtained.

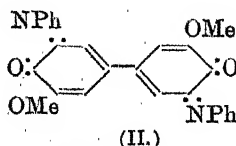
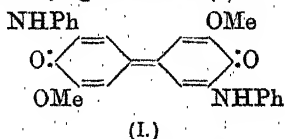
Methyl alcohol reacts with tetrachloro-*o*-benzoquinone, yielding a product, m. p. 198°, which cannot be reduced by sulphur dioxide, and hence is probably the methyl-monohemiacetal of hexachloro-*o*-quinocatechol ether.

J. J. S.

**Disodiophenolphthaloquinone or Disodioaciphenolphthalein.** C. FLEIG (*J. Pharm. Chim.*, 1909, [vi], 29, 465—471).—When phenolphthalein is added in excess to a solution of sodium hydroxide, the sodium derivative, formed has the composition  $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Na}_2$  (compare Meyer and Spengler, *Abstr.*, 1905, i, 440). It was obtained as a reddish-violet mass by evaporating the solution, and could not be prepared in a crystalline condition. Its behaviour with various solvents is described in the original. Its solution in water furnishes precipitates with many metallic salts, and these are usually unstable and are decomposed on boiling, yielding phenolphthalein and the corresponding metallic oxide. The possible systematic names for this substance are discussed, and the two given in the title are selected as most appropriate.

T. A. H.

**Nomenclature of the Lignones.** CARL LIEBERMANN (*Ber.*, 1909, 42, 1851—1852).—Bezdzik and Friedländer (this vol., i, 415) have applied the term "lignone" to certain binuclear quinones. The term "lignone blues" has been applied previously to the compounds obtained by the action of primary aromatic bases on coerulignone (Liebermann and Flatau, *Abstr.*, 1897, i, 224; Liebermann and Cybulski, *Abstr.*, 1898, i, 378), considered as derivatives of the aniline compound, lignone-blue (I).



The formula (II), containing two atoms of hydrogen less, is not definitely excluded.

In Friedländer's nomenclature, lignone-blue becomes bis-3-anilino-5-methoxybenzolinone, etc. This nomenclature is cumbersome, but may become necessary as the number of lignones increases.

C. H. D.

**Preparation of Leuco-derivatives of Hydroxyanthraquinones.** FARBERWERKE VORM. MEISTER, LUCIUS and BRÜNING (D.R.-P. 207668).—The sodium salt of leuco-1-amino-4-hydroxyanthraquinone-8-sulphonic acid, yellow needles, is produced on adding sodium hyposulphite to an alkaline solution of the anthraquinone derivative. The product is then transformed into the leuco-derivative of quinizarin-5-sulphonic acid by boiling with 10% hydrochloric acid. This reduction can be effected on the unsubstituted, or the hetero-nuclearly substituted, *p*-aminohydroxy- and *p*-diamino-anthraquinones.  
F. M. G. M.

**Preparation of Mercaptans of the Anthracene Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 206536).—Thiol and disulphide derivatives of anthraquinone are obtained by heating together the halogenated anthraquinones and the alkali sulphides or hydrosulphides. *α*-Thiolanthraquinone,  $C_{14}H_8O_2S$ , prisms, m. p. 187°, prepared from *α*-chloroanthraquinone and sodium sulphide in boiling alcohol, is accompanied by its oxidation product, the corresponding disulphide,  $(C_{14}H_7O_2)_2$ . The latter is reduced to the former by alkaline hyposulphite in alcoholic solution. *β*-Thiolanthraquinone, brown needles, is similarly obtained from *β*-chloroanthraquinone and sodium hydrosulphide.

*4*-Thiol-1-*p*-tolylaminoanthraquinone,  $C_7H_7 \cdot NH \cdot C_{14}H_8O_2 \cdot SH$ , dark blue needles, prepared from 1-chloro-4-*p*-tolylaminoanthraquinone and sodium hydrosulphide, yields on sulphonation a violet wool dye.  
F. M. G. M.

**Preparation of Mercaptans of the Anthraquinone Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 208640).—The thiocyanogen derivatives of the aromatic series are gradually converted into thiols either by heating with hydrochloric acid or by treatment with alkali hydrosulphides. These processes fail in the anthraquinone series, for hydrochloric acid does not hydrolyse the thiocyanogen group, whilst hydrosulphides reduce the carbonyl group. It has now been found that alkali hydroxides effect this transformation.

*α*-Thiocyanoanthraquinone (obtained from *α*-diazanthraquinone and potassium thiocyanate), when boiled with alcoholic sodium hydroxide, gives rise to the *α*-thiolanthraquinone,  $C_{14}H_7O_2 \cdot SH$ , which crystallises in yellow needles, m. p. 187°.

*β*-Thiolanthraquinone, pale yellow flakes, is similarly obtained from *β*-diazanthraquinone.  
F. M. G. M.

[The Sulphonation of Alizarin and Anthraflavic Acid.] R. WEDEKIND & Co. (D.R.-P. 205965).—When alizarin and anthraflavic acid are sulphonated with fuming acid (20–4%  $SO_3$ ) in the presence of mercury, the operation takes place more readily than in the absence of the metal, and new sulphonic acids are produced.  
F. M. G. M.

[Preparation of Bornyl and Menthyl Sulphuric Acids.] CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 208790).—It has been found that pure bornylsulphuric acid can be obtained (as its sodium salt) by the action of methylene sulphate on borneol in benzene solution, with subsequent treatment successively with barium and sodium carbonates.

Sodium bornyl sulphate is a colourless, very easily soluble salt, and resembles sodium menthyl sulphate, which is similarly prepared.

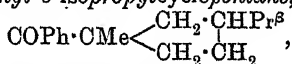
F. M. G. M.

Preparation of Menthyl  $\alpha$ -Bromoisovalerate. LÜDY & Co. (D.R.-P. 208789).—The introduction of bromine into menthyl isovalerate enhances the specific action of the drug in hysteria and neurasthenia.

Menthyl  $\alpha$ -bromoisovalerate, colourless, syrupy liquid, b. p. 150—160°/50 mm. and 205—208°/760 mm., is prepared by mixing, even in the cold, or more rapidly on warming, menthol and  $\alpha$ -bromoisovaleryl chloride (obtained by direct bromination of isovaleryl chloride).

F. M. G. M.

Synthesis of Derivatives of Racemic Fenchone. LOUIS BOUVEAULT and LEVALLOIS (*Compt. rend.*, 1909, 148, 1399—1401. Compare Abstr., 1908, i, 134, 193; 1909, i, 108).—The chloride of dihydrocampholenic acid has been obtained as a colourless liquid, b. p. 98°/16 mm. When treated with benzene in presence of aluminium chloride, it yields 3-benzoyl-1-isopropylcyclopentane,  $C_{15}H_{20}O$ , a pale yellow liquid, b. p. 166°/12 mm., the oxime of which has m. p. 128°. When treated with sodamide and methyl iodide the benzoyl derivative yields 1-benzoyl-1-methyl-3-isopropylcyclopentane,



b. p. 172°/15 mm. The oxime occurs in needles, m. p. 96·5°. Treatment of the methylketone with sodamide leads to the formation of benzene and 1-methyl-3-isopropylcyclopentane-1-carboxylamide, which should be identical with *r*-dihydrofencholenamide if the constitution previously ascribed to this compound is correct. The natural product has m. p. 116°, whilst the synthetic amide has m. p. 109°; it is probable, however, that the low m. p. is due to the presence of an isomeric compound.

W. O. W.

Preparation of Mixed Santalyl Esters of Dibasic Acids. J. D. RIEDEL (D.R.-P. 208637).—Methyl santalylsuccinate, an oil,  $D_{25}^{20}$  1·058, is prepared by treating santalol or sandal wood oil with succinic anhydride at 100—120°, and then alkylating the resulting santalylsuccinic acid with methyl sulphate and aqueous potassium hydroxide.

Methyl santalylphthalate, pale yellow oil,  $D_{25}^{20}$  1·085, is similarly obtained from santalylphthalic acid, methyl *p*-toluenesulphonate, and aqueous potassium hydroxide.

Methyl santalylcamphorate, pale yellow oil,  $D_{25}^{20}$  1·04, is produced by condensing santalol with camphoric anhydride and alkylating the intermediate santalylcamphoric acid.

F. M. G. M.

Constitution of Camphor and Its Derivatives. X. Electrolytic Reduction of Camphorcarboxylic Acid to *cis*- and *cis-trans*-Borneolcarboxylic Acids. Bornylenecarboxylic Acid (Preparation of Pure Bornylene). XI. Relationship of the Camphylglycols to the Borneolcarboxylic Acids. JULIUS BREDT (*Annalen*, 1909, 366, 1—70).—An investigation of the isomeric borneolcarboxylic acids obtained by the electrolytic reduction of camphorcarboxylic acid (compare Abstr., 1906, i, 680). It is shown that the two acids are *cis*- and *cis-trans*-isomerides, but although they have the same chemical constitution, nevertheless they behave differently towards an alkaline solution of potassium permanganate; the *cis*-acid, m. p. 102—103°, is readily and completely oxidised to camphoric acid, whilst the *cis-trans*-isomeride, m. p. 171°, remains unaltered when treated similarly. On the other hand, both acids yield camphoric acid when oxidised with nitric acid, and yield the same bornylenecarboxylic acid when subjected to dry distillation. The *cis*-acid is converted into the *cis-trans*-acid by acetyl chloride.

The acid described in the previous communication (*loc. cit.*) as dehydroborneolcarboxylic acid (camphenecarboxylic acid) is shown to be bornylenecarboxylic acid, since it yields camphoric acid when oxidised, and by suitable treatment gives rise to bornylene. The addition of hydrogen chloride or hydrogen bromide to bornylenecarboxylic acid takes place in the usual manner, that is, the halogen enters the  $\beta$ -position to the carboxyl group when the solvent employed is glacial acetic acid. When aqueous acids are employed, however, a chloro- or bromo-camphanecarboxylic acid is obtained. The latter have the same composition as those obtained by using glacial acetic acid, but have different properties; when heated with alkalis they yield a hydroxy-acid isomeric, but not identical, with either of the borneolcarboxylic acids obtained by the reduction of camphorcarboxylic acid. The nature of the isomerism is not yet clear.

The  $\beta$ -halogencamphanecarboxylic acids, prepared in glacial acetic acid, when treated with alkali yield bornylenecarboxylic acid, and also bornylene, which has been obtained in a state of purity for the first time. A lactone is also formed simultaneously as the result of intramolecular rearrangement.

The view previously advanced (*loc. cit.*), that the borneolcarboxylic acid, m. p. 170—171°, is probably related to *trans*-camphylglycol, m. p. 117—118°, as a hydroxy-acid to its glycol, is shown to be correct, since the *trans*-glycol is converted by oxidation with potassium permanganate into borneolcarboxylic acid, m. p. 170—171°. It has also been found possible to isolate an isomeric camphylglycol, m. p. 87°, corresponding with the borneolcarboxylic acid, m. p. 102—103°.

[With HERMANN SANDKUHLE.]—*cis*-Borneolcarboxylic acid,  $C_{11}H_{18}O_3$ , is far more soluble in toluene at the ordinary temperature than at 0°, and may be separated from the isomeride, m. p. 171°, by making use of this property. It crystallises in large, transparent, colourless prisms, m. p. 101°; the crystalline calcium salt,  $(C_{11}H_{17}O_3)_2Ca \cdot 2H_2O$ , is more soluble in cold than in hot water; the affinity constant  $K = 0.0105$ .

*cis-trans*-Borneolcarboxylic acid, m. p. 171°, has an affinity constant

$K = 0.00255$ . The acetate,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{CH} \cdot \text{OAc} \end{smallmatrix}$ , obtained by the action of acetyl chloride (two parts) on either *cis*- or *cis-trans*-borneolcarboxylic acid (1 part), forms colourless crystals, m. p.  $122-123^\circ$ . When four parts of acetyl chloride are employed, an amorphous, indifferent substance is obtained, which is probably a mixture of *acetylborneolcarboxylic acid anhydride*,  $(C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}- \\ | \\ \text{CH} \cdot \text{OAc} \end{smallmatrix})_2\text{O}$ , and an *anhydride of cis-trans-borneolcarboxylic acid*,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO} \cdot \text{O} \cdot \text{CH} \\ | \quad \quad | \\ \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{CH} \end{smallmatrix} > C_8H_{14}$ .

An acid,  $C_{11}H_{18}O_3$ , m. p.  $126^\circ$ , was isolated from the product obtained by the electrolytic reduction of camphorcarboxylic acid; the calcium salt,  $(C_{11}H_{17}O_3)_2Ca$ , was analysed. It is possible that this acid is another of the four possible stereoisomeric borneolcarboxylic acids.

*Bornylene-carboxylic acid*,  $C_{11}H_{16}O_2$ , m. p.  $112-113^\circ$ , b. p.  $158^\circ/13$  mm., is most readily prepared by the distillation of acetylborneolcarboxylic acid at  $157^\circ/14$  mm.; the *anhydride*,  $C_{22}H_{30}O_3$ , is a white, crystalline substance, m. p.  $97^\circ$ , b. p.  $220-225^\circ/15$  mm. The acid, when oxidised with an aqueous  $2\frac{1}{2}\%$  solution of potassium permanganate, yields camphoric acid, hydroxyoxidocamphanecarboxylic acid, and other acids which have not yet been investigated. *Hydroxyoxidocamphanecarboxylic acid* (annexed formula) crystallises in white leaflets, m. p.  $208-209^\circ$ ; the calcium salt,  $(C_{11}H_{15}O_4)_2Ca \cdot 4H_2O$ , crystallises in needles.

$C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{CO}_2\text{H} \\ | \quad \quad | \\ \text{O} \quad \quad \text{O} \\ | \quad \quad | \\ \text{C} \cdot \text{OH} \end{smallmatrix}$  yields camphoric acid, hydroxyoxidocamphanecarboxylic acid, and other acids which have not yet been investigated. *Hydroxyoxidocamphanecarboxylic acid* (annexed formula) crystallises in white leaflets, m. p.  $208-209^\circ$ ; the calcium salt,  $(C_{11}H_{15}O_4)_2Ca \cdot 4H_2O$ , crystallises in needles.

$\beta$ -Bromocamphanecarboxylic acid,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{CHBr} \end{smallmatrix}$ , is obtained by the action of hydrogen bromide in glacial acetic acid on bornylene-carboxylic acid; it crystallises in large needles, m. p.  $90-91^\circ$ ; the sodium salt forms large leaflets. Small quantities of a *hydroxy-acid*,  $C_{11}H_{18}O_3$ , are obtained in the preparation of the preceding acid; it crystallises in slender, felted needles, m. p.  $169^\circ$ , and yields a *dehydro-acid*,  $C_{11}H_{16}O_2$ , when its aqueous solution is boiled for some time; the latter substance crystallises in needles, m. p.  $55^\circ$ .

$\beta$ -Chlorocamphanecarboxylic acid,  $C_{11}H_{17}O_2Cl$ , prepared in a similar manner, has m. p.  $84-85^\circ$ .

$\alpha$ -Bromocamphanecarboxylic acid,  $C_{11}H_{17}O_2Br$ , forming granular crystals, m. p.  $157^\circ$ , is obtained, together with the  $\beta$ -bromo-acid just described, by the action of concentrated hydrobromic acid on bornylene-carboxylic acid; it is converted by a hot solution of sodium carbonate into a *hydroxy-acid*,  $C_{11}H_{18}O_3$ , which forms granular crystals, m. p.  $176^\circ$ , and does not yield camphoric acid when hydrolysed.

The  $\beta$ -halogenated camphanecarboxylic acids when heated with aqueous alkalis yield a mixture of bornylene, bornylenecarboxylic acid, and  $\gamma$ -hydroxycarbohydrocamphenolactone, the proportions of which vary with the conditions employed. The production of bornylene is favoured by using excess of alkali and heating rapidly to a high temperature under pressure.

Bornylene obtained by this method is a crystalline substance, m. p.

113°, b. p. 146°/740 mm.,  $[\alpha]_D^{18} - 21.69^\circ$  ( $c = 10.45$  in toluene),  $[\alpha]_D^{18} - 26.96^\circ$  ( $c = 4.42$  in methyl alcohol) (compare Wagner, Abstr., 1900, i, 554; Tschugaeff, Abstr., 1905, i, 71).

$\gamma$ -Hydroxycarbohydrocamphenolactone, having the annexed formula, forms colourless crystals, m. p. 183°, b. p. 145—147°/12 mm.; the calcium salt,  $(C_{11}H_{17}O_3)_2Ca$ , crystallises with  $H_2O$ , which is liberated when the salt is exposed to the air. The lactone is oxidised by hot nitric acid (D 1.27), yielding camphenilol- $\gamma$ -dicarboxylic acid, the lactone (annexed formula) of which forms long, feathery crystals, m. p. 230°; the barium salts,  $(C_{11}H_{13}O_4)_2Ba$  and  $(C_{11}H_{14}O_5)_2Ba$ , were prepared and analysed; the latter is very unstable, being decomposed by carbon dioxide.

ortho-Camphanecarboxylic acid,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CH}_2 \end{smallmatrix}$ , is prepared by reducing  $\beta$ -bromocamphanecarboxylic acid with potassium amalgam; it is a crystalline substance, m. p. 90—91°, b. p. 153°/13 mm.

The reduction of hydroxymethylenecamphor with sodium and alcohol leads to the production of a mixture of *cis*-camphylglycol and *cis-trans*-camphylglycol (compare Farbwerke vorm. Meister, Lucius and Brining, Abstr., 1902, i, 299). The separation is effected by crystallisation from ethyl acetate. The *cis*-camphylglycol,  $C_{11}H_{20}O_2$ , separates out first as transparent, colourless needles, m. p. 87°. It is oxidised by potassium permanganate to camphoric acid, and when distilled yields bornylenecarbinol (dehydrocamphylglycol), crystallising in long needles, m. p. 67—68°, b. p. 119—121°/13 mm. The *cis-trans*-glycol does not lose water when treated in the same way as the *cis*-isomeride, and when oxidised with potassium permanganate yields *cis-trans*-borneolcarboxylic acid.

W. H. G.

**The Camphenilone Group. I. Camphenilol.** GUSTAV KOMPFA (*Annalen*, 1909, 366, 71—78).—An account of the preparation and properties of several compounds derived from camphenilone.

*Camphenilyl acetate*,  $C_9H_{15}OAc$ , prepared by the action of acetic anhydride on camphenilol, is a colourless liquid having an intense ethereal odour, b. p. 95—97°/17 mm.,  $D_4^{20} 0.9974$ ,  $n_D^{20} 1.4628$ . *Camphenilylphenylurethane*,  $C_9H_{15}O \cdot CO \cdot NHPh$ , prepared from camphenilol and phenylcarbimide, crystallises in slender needles, m. p. 99.5°. *Camphenilyl hydrogen phthalate*,  $CO_2H \cdot C_6H_4 \cdot CO_2 \cdot C_9H_{15}$ , obtained by heating camphenilol with phthalic anhydride at 150—180°, forms short, broad crystals, m. p. 148.5—149°.

*Camphenilylamine*,  $C_8H_8 \begin{smallmatrix} \text{CMe}_2 \\ \text{CH} \cdot \text{NH}_2 \end{smallmatrix}$ , prepared by reducing campheniloneoxime with sodium and alcohol, is obtained as a crystalline mass, m. p. 90—92° (in a sealed tube), b. p. 180—185.5°, having an odour reminiscent of bornylamine and putrid fish offal; the *hydro*-

*chloride*,  $C_9H_{15} \cdot NH_2 \cdot HCl$ , forms long, stout needles, which do not melt at  $200^\circ$ ; the *platinichloride*,  $C_{18}H_{34}N_2 \cdot H_2PtCl_6$ , crystallises in pale yellow, thin tetrahedra, which become black, but do not melt, at  $230-235^\circ$ ; the *picrate*,  $C_{15}H_{20}O_7N_4$ , crystallises in yellow needles, m. p.  $205-207^\circ$ .

*Camphenilylcarbamide*,  $NH_2 \cdot CO \cdot NH \cdot C_9H_{15}$  obtained by the action of potassium cyanate on camphenilylamine hydrochloride in aqueous solution, forms small, slender, glistening needles, m. p.  $167.5-168^\circ$ . *Camphenilylphenylthiocarbamide*,  $NHPh \cdot CS \cdot NH \cdot C_9H_{15}$ , prepared by the action of phenylthiocarbimide on an ethereal solution of camphenilylamine, crystallises in square prisms, m. p.  $154^\circ$ .

W. H. G.

**New Method for the Hydration of Pinene. II. Partial Proximate Analysis and Purification of Crude Pinene. III. Examination of the Alcohols Formed and Origin of Fenchyl Alcohol.** PHILIPPE BARBIER and VICTOR GRIGNARD (*Bull. Soc. chim.*, 1909, [iv], 5, 512-519, 519-526).—The method already described (*Abstr.*, 1908, i, 94), depending on the action of an aqueous solution of benzenesulphonic acid on pinene in presence of acetic acid, has been improved by the addition of acetic anhydride to the reaction mixture, whereby the time necessary for completion has been reduced from twelve to from one and a-half to two hours.

The hydrocarbons recovered unchanged from the first hydration consist mainly of pinene, which is purer than the initial product, since on oxidation it yields only traces of nopinic acid. It contains in addition a hydrocarbon of low b. p., which is unsaturated, but is not bornylene. In order to eliminate pinene from the recovered unchanged products, these were subjected to the hydration process three times in succession. At this stage the recovered hydrocarbons still contained the hydrocarbons of low b. p., some terpadienes, camphene, and some pinene, the last-mentioned being now partly racemised. After two further hydrations the pinene and terpadienes were completely removed. The residual hydrocarbons from 4 kilos. of crude pinene after these six hydrations consisted of the following fractions: b. p.  $148-152^\circ$  (6 grams), b. p.  $152-154^\circ$  (12 grams), b. p.  $154-158^\circ$  (25 grams), and b. p.  $158-161^\circ$  (12 grams). The last three deposited partly racemic camphene on cooling. This had m. p.  $42^\circ$ , and optical rotation  $-0.40^\circ$  in a 100 mm. tube. The mother liquor from the camphene and the first fraction (b. p.  $148-152^\circ$ ) on treatment with sulphuric acid were largely polymerised, and left a saturated product,  $C_{10}H_{18}$ , b. p.  $157-160^\circ$ .

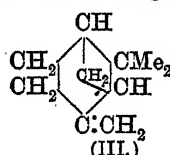
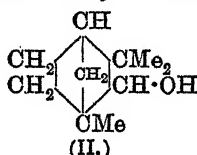
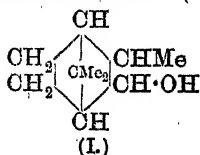
The terpadienes in the hydrocarbons recovered from the fourth hydration appeared to consist of *l*-limonene, dipentene, and possibly terpinolene, all probably produced by the dehydration of  $\alpha$ -terpineol.

From a consignment of *l*-rotatory turpentine oil of unknown origin, a low boiling fraction consisting of methylcyclohexane and dimethylcyclohexane was isolated by a combination of fractional distillation and the hydration process. No opinion is offered as to whether or not these are normal constituents of turpentine oil.

The products of hydration are a series of alcohols, which occur in the

reaction mixture as acetates, and are isolated by distilling off the unchanged hydrocarbons under reduced pressure and saponifying the residue boiling above 170°. This method answers for the first three hydrations, but after that stage the quantity available is small, and separation is effected by converting the alcohols into their acid phthalates. The products of the first hydration are *l*- $\alpha$ -terpineol mixed with a little of the racemic form, *d*-fenchyl alcohol with a little of the racemic form, and a crystalline product, m. p. 195—200°, which is laevorotatory and gives a phenylurethane, m. p. 139—142°. This may be a mixture of borneol and isoborneol, or possibly a new alcohol. No new products are then obtained until the fourth hydration, when a mixture of borneol and isoborneol (m. p. 195—196°; phenylurethane, m. p. 130°) is produced. In the latter hydrations a small quantity of a liquid alcohol is also formed.

It is suggested that the fenchyl alcohol and the alcohol melting at 195—200° result from the hydration of nopinene, since they are no longer formed when this has disappeared. Wallach's formula for fenchyl alcohol (I) does not account for such a formation, but Semmler's (II) does if the formula generally accepted for nopinene be written as follows (III), since it may be assumed that the "bridge" is



broken, the double linking hydrated, and the "bridge" re-formed.

T. A. H.

**Elimination of Hydrogen Chloride from *d*-Limonene Nitrosochloride. A New Carvoxime.** ERNST DEUSSEN and ALFRED HAHN (*Chem. Zentr.*, 1909, i, 1237; from *Zeitsch. Riech.-Geschmackstoffe*, 1909, 1, 25—26).—When *d*-limonene nitrosochloride is treated with 1 mol. of sodium methoxide, the *l*-carvoxime formed is accompanied by a considerable quantity of an oil, which has approximately the same composition. This oil is slightly dextrorotatory, or optically inactive, or slightly laevorotatory, owing to varying quantities of a *d*-carvoxime being present in admixture with *l*-carvoxime. By means of a difference in solubility of the benzoyl compound, a separation of the two oximes was effected; the *d*-benzoylcarvoxime purified from alcohol has m. p. 77° and  $[\alpha]_D + 75.3^\circ$ , and is unimolecular in benzene solution.

*d*-Carvoxime,  $\text{C}_{10}\text{H}_{14} \cdot \text{N} \cdot \text{OH}$ , crystallises from aqueous alcohol in glistening needles, m. p. 57—58°;  $[\alpha]_D + 68.3^\circ$  in benzene solution. It may be obtained from *d*-limonene  $\alpha$ - or *d*-limonene  $\beta$ -nitrosochloride, and is called  $\beta$ -carvoxime to distinguish it from the well known *l*-carvoxime or  $\alpha$ -compound, m. p. 72°. When heated with dilute sulphuric acid it yields an oil smelling strongly of carvone.

J. V. E.

**Terpinenes.** IWAN KONDAKOFF (*J. pr. Chem.*, 1909, 79, 497—505).—A review of recent work on terpinene. The conclusion is drawn

that the terpinene prepared by the methods hitherto described is always a mixture of isomerides. W. H. G.

**Cubebin. II and III.** EFISIO MAMELI (*Gazzetta*, 1909, 39, i, 477—493, 494—508. Compare Abstr., 1908, i, 20).—The action of a large number of substances, especially of halogen hydracids in acetic acid solution, on cubebin yield cubebin ether, m. p. 78° (compare Pomeranz, Abstr., 1888, 162, 1100), which is formed by dehydration of cubebin,  $2C_{10}H_{10}O_3 = H_2O + C_{20}H_{18}O_5$ . Cubebin and its derivatives undergo a series of reactions similar to those of the pinacones and their derivatives; just as the pinacone yields by dehydration a pinacolin which gives a pinacolic alcohol on reduction, so also cubebin yields cubebin ether, and this, on reduction, a monohydric alcohol (*vide infra*).

Cubebin ether,  $[\alpha]_D + 23.03^\circ$ , does not contain carbonyl or hydroxyl oxygen, and has the probable formula:  $C_6H_5O(C_6H_3O_2CH_2)_2$ .

**Cubebinol**,  $OH \cdot C_6H_5(C_6H_3O_2CH_2)_2$ , prepared by reducing cubebic acid by means of sodium and alcohol, crystallises from a mixture of light petroleum and benzene in spherical tufts of silky, white needles, m. p. 92°,  $[\alpha]_D + 34.81^\circ$ . Addition of 4Br yields a bromide, m. p. 70—85°, which could not be purified. Cubebinol rapidly decolorises permanganate, the only products observed being carbon dioxide, an acid obtained only as a syrup, and piperonylic acid (?). It reduces Nessler's reagent and ammoniacal silver solution, but not Fehling's solution. Its *acetyl* derivative,  $C_{22}H_{22}O_6$ , crystallises from alcohol in tufts of silky needles, m. p. 71°,  $\alpha_D + 23.12^\circ$ ; its *benzoyl* derivative,  $C_{27}H_{24}O_6$ , m. p. 154—155°,  $\alpha_D - 21.68^\circ$ , and its *phenylurethane*,  $C_{27}H_{26}O_6N$ , m. p. 154—155°, were also prepared.

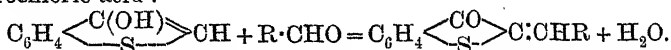
Measurements of the velocity of acetylation of cubebinol indicate that it is a primary alcohol. T. H. P.

**Composition of Tannin.** LEO F. ILJIN (*Ber.*, 1909, 42, 1731—1735).—The following methods have been used for the purification of commercial tannin. (1) Dialysis in a parchment thimble, conversion of the dialysed product into the lead derivative, and decomposition of this with hydrogen sulphide. The product was finally precipitated by the addition of chloroform to the solution of the tannin in alcohol and ethyl acetate. (2) Modification of Walden's method (Abstr., 1899, i, 212). (3) Rosenheim and Schidrowitz's method (Trans., 1898, 73, 882). (4) Fractional precipitation of the aqueous solution with sodium chloride. (5) Fractional precipitation of the solution in alcohol and ethyl acetate with chloroform.

All the products had relatively high rotations,  $[\alpha]_D^{20.5} + 65—75^\circ$ , and the percentage composition did not agree with that of a digallic acid (Nierenstein, Abstr., 1908, i, 90, 897). J. J. S.

**Dyes of the Thionaphthen Series.** PAUL FRIEDLÄNDER (*Monatsh.*, 1909, 30, 347—354).—The analogy of 2-hydroxythionaphthen to  $\alpha$ -naphthol on the one hand and to indoxyl on the other (Abstr., 1906, i, 378; 1907, i, 334) is further illustrated by the formation of thioindogenides and hydroxyazo-compounds.

Like indoxyl, it condenses with aromatic aldehydes to form thioindogenides of almost the same colour as the corresponding indogenide. The yellow colour is intensified, but not changed essentially, by the presence of auxochromic groups in the aldehyde molecule. The condensation is effected by warming equal molecular quantities of 2-hydroxythionaphthen and an aldehyde in light petroleum or solvent naphtha, or in alcohol or glacial acetic acid with a few drops of hydrochloric acid:

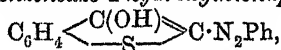


In practice it is convenient to use sodium 2-hydroxythionaphthen-1-carboxylate, which loses carbon dioxide when heated in glacial acetic acid, yielding 2-hydroxythionaphthen.

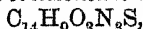
Thioindogenides have been prepared from the following aldehydes and ketones:

Thioindogenide from	M. p.	Colour.	Coloration with conc. $\text{H}_2\text{SO}_4$ .	Colour of Na salt in solution.
Benzaldehyde .....	127°	Yellow	Cherry-red	—
<i>o</i> -Nitrobenzaldehyde ...	171	Orange-red	Bluish-violet	—
<i>m</i> -Nitrobenzaldehyde ...	223—224	Yellow	Bluish-violet	—
<i>p</i> -Nitrobenzaldehyde ...	231	Orange-red	—	—
Salicylaldehyde .....	209	Orange-yellow	—	Carmine-red
<i>m</i> -Hydroxybenzaldehyde	212	Citron-yellow	—	Pale yellow
<i>p</i> -Hydroxybenzaldehyde	262	Orange-yellow	—	Orange-red
Protocatechualdehyde ..	above	Brownish	Cherry-red	Reddish-violet
	280	Orange-yellow		
2:4-Dihydroxybenzaldehyde .....	—	Orange-brown	—	Bluish-red
Piperonal .....	207	Yellow	Bluish-violet	—
Fluorenone .....	200—202	Brick-red	Olive-green	—

2-Hydroxythionaphthen couples readily in alkaline solution with diazonium salts. 1-Benzeneazo-2-hydroxythionaphthen,



m. p. 191—192°, forms orange-yellow needles, and is soluble in sodium hydroxide solution. 1-*p*-Nitrobenzeneazo-2-hydroxythionaphthen,



forms sparingly soluble, orange-red needles, gives a bluish-violet solution in sodium hydroxide or hot sodium carbonate, and develops a cherry-red coloration with concentrated sulphuric acid. C. S.

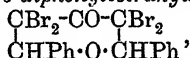
**Bromination of Certain Tetrahydropyrone Compounds.** W. SCHTYAN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 477—482).—By the formation of two double linkings in the nucleus of tetrahydropyrone compounds, the author shows that the latter contain the pyrone ring.

Attempts to oxidise ethyl diphenyltetrahydropyrone-3-carboxylate,  $\text{C}_{23}\text{H}_{24}\text{O}_6$ , m. p. 114—126°, were unsuccessful.

Ethyl 3:5-dibromo-2:6-diphenyltetrahydropyrone-3:5-dicarboxylate,  $\text{CO}_2\text{Et} \cdot \text{CBr} \cdot \text{CO} \cdot \text{CBr} \cdot \text{CO}_2\text{Et}$ , prepared by brominating ethyl diphenyltetrahydropyrone-3-carboxylate, separates from acetic acid in crystals,

m. p. 171° (decomp.), and has the normal molecular weight in freezing nitrobenzene. Removal of 2HBr from this compound by means of pyridine in presence of silver nitrate yields ethyl 2:6-diphenylpyrone-3:5-dicarboxylate (compare Dünschmann and Pechmann, *Abstr.*, 1891, 673), m. p. 140.5—141°, which, with ammonia, gives the ester, m. p. 195°, obtained by Petrenko-Kritschenko and Petroff (*Abstr.*, 1908, i, 564); hydrolysis of the ester yields the acid, m. p. 250—258°.

3:3:5:5-Tetrabromo-2:6-diphenyltetrahydropyrone,



obtained by the action of bromine on sodium diphenyltetrahydropyronecarboxylate, crystallises from alcohol in monoclinic plates, m. p. 165—171°.

Bromination of diphenyltetrahydropyrone, m. p. 130°, in acetic acid yields a *tetrabromo*-derivative, which separates from alcohol in small, radiating, monoclinic crystals, m. p. 197—200°, and is apparently isomeric with the preceding compound, m. p. 165—171°.

T. H. P.

**Cinchona Alkaloids.** GEORG RÖHDE (*Ber.*, 1909, 42, 2182).—Polemical in regard to the paper by Rabe (*this vol.*, i, 408).

P. H.

**Preparation of Easily Soluble Double Salts of Sodium Theobromine.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 208188).—Therapeutically important theobromine compounds are obtained by combining sodium theobromine with the alkali halides.

*Sodium theobromine-sodium chloride* results from the mixing of concentrated solutions of its generators. This and other double salts of sodium theobromine with alkali halide are white, easily soluble powders, with a bitter taste and an alkaline reaction. They dissolve in dilute alcohol and glycerol, but are insoluble in absolute alcohol and other anhydrous solvents.

F. M. G. M.

**Fission of Disulphides with Neighbouring Double Linkings.** EMIL FROMM (*Ber.*, 1909, 42, 1945—1959).—The ready formation of thiocarbamides from carbon disulphide and aromatic amines in the presence of hydrogen peroxide is explained by Braun by the intermediate production of a thiuram disulphide, which breaks down into sulphur, carbon disulphide, and the thiocarbamide (*Abstr.*, 1900, i, 644). Since disulphides with neighbouring double linkings are decomposed by water, alkalis, or amines with elimination of sulphur, the author has suggested that thiuram disulphides, which are disulphides of this type, are hydrolysed by water:  $\text{S}_2(\text{CS}\cdot\text{NHPh})_2 + \text{H}_2\text{O} = \text{S} + \text{NHPh}\cdot\text{CS}\cdot\text{SH} + \text{NHPh}\cdot\text{CS}\cdot\text{OH}$ ; by the decomposition of these products, aniline and phenylthiocarbimide are formed, from which the thiocarbamide is produced (*Abstr.*, 1906, i, 656). Braun (*Abstr.*, 1907, i, 123) objects to this explanation on the ground that hydrogen sulphide, but not carbon disulphide, is formed in the preparation of the thiocarbamide. In the present paper the author, whilst pointing out that Braun's objection does not harmonise with his own explanation of the

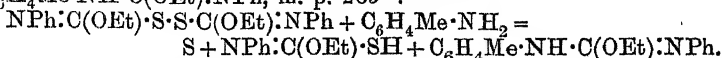
formation of the thiocarbamide (see above), withdraws his previous explanation, since he has obtained evidence that the fission of the thiuram disulphide is effected, not by water, but by the excess of the aromatic amine in accordance with the scheme:  $S_2(CS \cdot NHR)_2 + 2R' \cdot NH_2 = S + NHR \cdot CS \cdot NHR' + NHR \cdot CS \cdot SH, NH_2R'$ . This simple reaction occurs only rarely, for example, piperidylthiuram disulphide and piperidine at  $120^\circ$  yield *dipiperidylthiocarbamide*,  $(C_5NH_{10})_2CS$ , m. p.  $58^\circ$ , and piperidine piperidylthiocarbamate (Ehrenberg, Abstr., 1887, 1026). A disturbing influence is sometimes introduced by the decomposition of the arylthiocarbamate into hydrogen sulphide and a thiocarbamide; thus piperidylthiuram disulphide and aniline in boiling alcohol yield sulphur, hydrogen sulphide, and phenylpiperidylthiocarbamide. Another complication is caused by one amine ousting another from the disulphide. Such an instance is found in Braun's diphenyldimethylthiuram disulphide (Abstr., 1902, i, 271), which, reacting with piperidine at  $110^\circ$  or with aniline or phenylhydrazine in boiling alcohol, has the two  $-NMePh$  groups replaced by the amine, so that with piperidine, dipiperidylthiocarbamide, piperidine piperidylthiocarbamate and sulphur are formed, with aniline, hydrogen sulphide, sulphur and diphenylthiocarbamide, and with phenylhydrazine, hydrogen sulphide, sulphur and diphenylthiocarbazine. The action of phenylhydrazine on piperidylthiuram disulphide is still more complex, the products being hydrogen sulphide, ammonia, and phenylthiosemicarbazine. The initial decomposition of the disulphide follows the rule, sulphur, piperidylphenylhydrazinothiocarbamide and phenylhydrazine piperidylthiocarbamate being formed; the last breaks down into hydrogen sulphide and another molecule of piperidylphenylhydrazinothiocarbamide, whilst the sulphur, acting on the excess of phenylhydrazine, generates ammonia, which displaces the piperidyl group from the thiocarbamide, forming phenylthiosemicarbazine.

Thiuram disulphides are attacked most easily by phenylhydrazine or aniline, less readily by piperidine, and with the greatest difficulty by methylaniline. This behaviour explains why piperidylthiuram disulphide (Ehrenberg, *loc. cit.*) and diphenyldimethylthiuram disulphide (Braun, *loc. cit.*) are readily prepared, whilst phenylthiuram disulphide cannot be obtained, being attacked by the excess of aniline and forming diphenylthiocarbamide.

The decomposition of thiuram disulphide (thiocarbamic disulphide) by aniline has been investigated by Klason (Abstr., 1887, 1025), and his results are confirmed by the author. The decomposition of the disulphide by phenylhydrazine in the cold yields sulphur, ammonia, hydrogen sulphide, phenylthiosemicarbazine, and diphenylthiocarbazine. The formation of the products obtained by these two decompositions is in perfect harmony with the author's scheme of the fission of a thiuram disulphide by an amine.

[With ADOLF ROESICKE and MAX TAUSENT.]—Jacobson's phenylthiourethane sulphide (Abstr., 1886, 876), which is more readily obtained by oxidising phenylthiourethane, dissolved in sodium hydroxide, D 1.3, and a little alcohol, by iodine in potassium iodide, is a disulphide with neighbouring double linkings, and its fission by *p*-toluidine at  $125^\circ$  results in the formation of sulphur, phenylthiourethane, *phenyl-*

*p*-tolylcarbamide, m. p. 231°, and phenyl-*p*-tolylethyl- $\psi$ -carbamide,  $C_6H_4Me \cdot NH \cdot C(OEt) : NPh$ , m. p. 265°:



The phenyl-*p*-tolylcarbamide is formed by the action of phenylthiourethane on the  $\psi$ -carbamide, whereby phenyl-*p*-tolylcarbamide and ethyl phenyliminothiocarbonate are produced, the presence of the latter being detected by warming the mixture with hydrochloric acid at 150°, whereby ethyl mercaptan is liberated (compare Liebermann, *Annalen*, 1881, 207, 149).

C. S.

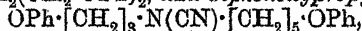
The Fission of Cyclic Bases by Cyanogen Bromide. II. JULIUS VON BRAUN (*Ber.*, 1909, 42, 2035—2057. Compare Abstr., 1907, i, 960).—The breaking of the ring in cyclic bases by cyanogen bromide extends to all those compounds,  $X \triangleleft N \cdot R$ , in which R is a homologue of methyl. Methyl, allyl, and benzyl compounds are not broken down. A number of piperidine derivatives have now been examined. In each case, the initial compound,  $C_5NH_{10} \cdot X$ , is treated with cyanogen bromide, and the relative quantities of the three products,  $C_5NH_{10} \cdot CN$ ,  $XBr$ , and  $Br \cdot [CH_2]_5 \cdot NX \cdot CN$ , estimated. The brominated compounds are isolated by replacing the bromine by the groups  $NHR$  or  $NR_2$ . The cyanamides are best converted into guanidines.

Piperidinocyanamide only reacts with difficulty with ammonium salts, but readily with the salts of primary amines. The *guanidine* derivative from *p*-tolylamine,  $C_5NH_{10} \cdot C(NH) \cdot NH \cdot C_6H_4Me$ , has m. p. 115°; the *picrate*, m. p. 132°, and *platinicyanide*, m. p. 205° (decomp.), are described. The compound from aniline does not crystallise well; its *picrate* has m. p. 107°, and *platinicyanide*, m. p. 195°.

*Diperidinoguanidine*,  $NH \cdot C(C_5NH_{10})_2$ , is a colourless liquid, b. p. 175—177°/12 mm.; the *picrate*, m. p. 148°, and *platinicyanide*, m. p. 192° if slowly heated.

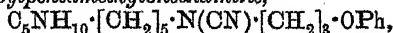
$\gamma$ -Phenoxypropylpiperidine,  $C_5NH_{10} \cdot [CH_2]_3 \cdot OPh$  (Gabriel and Stelzner, Abstr., 1896, i, 703), is best prepared from piperidine and phenyl iodopropyl ether. It forms an oil, b. p. 172°/13 mm.; the *hydriodide* has m. p. 183°, and the *methiodide*, m. p. 159—160°. It gives a mixed oily product with cyanogen bromide, which on hydrolysis with hydrobromic acid yields  $\gamma$ -bromopropyl- $\epsilon$ -bromoamylcyanamide,  $Br[CH_2]_3 \cdot N(CN) \cdot [CH_2]_5 \cdot Br$ , an oil. At higher temperatures the hydrolysis gives rise to an impure *hydrobromide* of  $\gamma$ -bromopropyl- $\epsilon$ -bromoamylamine,  $Br[CH_2]_3 \cdot NH \cdot [CH_2]_5 \cdot Br$ , HBr, m. p. 202—210°.

Sodium phenoxide converts the oily product into  $\alpha$ -propyleneglycol diphenyl ether,  $CH_2(CH_2 \cdot OPh)_2$ , and *diphenoxypropylcyanamide*,



m. p. 36°. The cyano-group is attacked by acids with great difficulty.

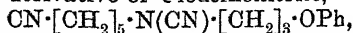
The oily product condenses with bases. Piperidine forms *piperidyl-cyanophenoxypropylpentamethylenediamine*,



a yellow, basic liquid. The salts are oily. The product from methyl-aniline contains *phenoxypropylmethylaniline*,  $OPh \cdot [CH_2]_3 \cdot NMePh$ , b. p.

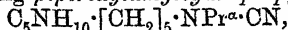
217°/10 mm., *picrate*, m. p. 111°, and  $\epsilon$ -cyano- $\epsilon$ -phenoxy- $\alpha$ -phenyl- $\alpha$ -methylpropylpentamethylenediamine. Aniline forms the corresponding *phenyl* derivative,  $\text{NHPh} \cdot [\text{CH}_2]_5 \cdot \text{N}(\text{CN}) \cdot [\text{CH}_2]_3 \cdot \text{OPh}$ , a yellowish-red, viscous liquid, yielding oily salts and derivatives.

Potassium cyanide also condenses with the oil, yielding  $\gamma$ -phenoxy-butyronitrile and a derivative of  $\epsilon$ -leucinonitrile,



which on hydrolysis forms the corresponding *derivative* of leucine, m. p. 131°.

1-Propylpiperidine, best prepared from dibromopentane and propylamine, reacts violently with cyanogen bromide. The product reacts with piperidine, forming *piperidylamylecyanopropylamine*,



an oil, from which the cyano-group may be removed, yielding *piperidylamylpropylamine*, b. p. 146—150°/12 mm.; *picrate*, m. p. 175°; *platinichloride*, m. p. 228° (decomp.).

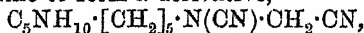
Ethyl  $\beta$ -piperidylpropionate (Wedekind, *Ber.*, 1899, 32, 727) has b. p. 230°; the *picrate*, m. p. 127°; *hydrobromide*, m. p. 154°. The product of the action of cyanogen bromide condenses with piperidine, forming diperidylguanidine and other products.

$\gamma$ -Phthaliminopropylpiperidine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot [\text{CH}_2]_3 \cdot \text{C}_5\text{NH}_{10}$ , from bromopropylphthalimide and piperidine in the cold, forms white crystals, m. p. 50°; *picrate*, m. p. 190°. Cyanogen bromide forms  $\gamma$ -bromopropylphthalimide.

1-Ethylpiperidine and cyanogen bromide yield *piperidylamylecyanoethylamine*,  $\text{C}_5\text{NH}_{10} \cdot [\text{CH}_2]_5 \cdot \text{NEt} \cdot \text{CN}$ , b. p. 191—192°/11 mm.; the *amine* obtained on hydrolysis has b. p. 132°/10 mm.; *picrate*, m. p. 151°; *platinichloride*, m. p. 220°.

$\xi$ -Ethylaminoheptonic acid,  $\text{NHEt} \cdot [\text{CH}_2]_6 \cdot \text{CO}_2\text{H}$ , has m. p. 129—130°, and partly forms an internal anhydride on heating. The *platinichloride* has m. p. 117°.

Piperidylacetonitrile and cyanogen bromide form a product which reacts with piperidine to form a derivative,



a heavy oil (compare *Abstr.*, 1908, i, 675). *Piperidylacetonitrile picrate* has m. p. 157°.

C. H. D.

**Preparation of *N*-Substituted Aminomethyl Derivatives of Eugenol- and *iso*Eugenol-acetamides.** ALFRED EINHORN (D.R.-P. 208255).—The condensation products of the acetamides of eugenol and *isoeugenol* with formaldehyde and secondary aliphatic amines are basic substances possessing the property of producing local anaesthesia. This condensation may be effected either in one stage, or the methylol and dimethylol compounds may first be produced, and then condensed with the aliphatic bases.

*Eugenolacetopiperidylmethylamide*,

$\text{OMe} \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_{10}$ , crystals, m. p. 48—52° (*hydrochloride*, white needles, m. p. 142—144°), is prepared by boiling in alcoholic solution either (1) eugenol-acetamide, formaldehyde, and piperidine; (2) *N*-methylol-eugenol-

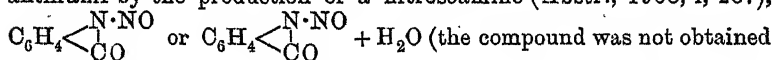
acetamide,  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{C}_3\text{H}_5)_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{OH}$ , and piperidine, or (3) eugenolacetamide and piperidomethanol,  $\text{C}_6\text{H}_9\text{N} \cdot \text{CH}_2 \cdot \text{OH}$ , or methylenedipiperidine,  $\text{CH}_2(\text{C}_5\text{H}_{10}\text{N})_2$ . Analogously constituted compounds are obtained by substituting diethylamine and other secondary bases for piperidine in the above condensation, and also from isoeugenolacetamide. F. M. G. M.

**Course of the Friedel-Craft Reaction with Unsymmetrical Polycarboxylic Acids.** ALFRED KIRPAL (*Monatsh.*, 1909, 30, 355—361).—The divergent results of the condensation of cinchomeric anhydride and benzene by aluminium chloride obtained by Philips (Abstr., 1894, i, 554), Freund (Abstr., 1898, i, 43), and Fulda (Abstr., 1900, i, 53) has induced the author to repeat the condensation. He obtains the two isomeric substances 4-benzoylnicotinic acid and 3-benzoylisonicotinic acid, of which the former is soluble in boiling water. The two acids are obtained separately by condensing 3-methyl cinchomeronate 4-chloride and 4-methyl cinchomeronate 3-chloride respectively with benzene and aluminium chloride. 4-Benzoylnicotinic acid has m. p.  $226^\circ$ , forms a hydrochloride,  $\text{C}_{13}\text{H}_9\text{O}_3\text{N} \cdot \text{HCl}$ , m. p.  $240^\circ$  (decomp.), and yields above its m. p. 4-benzoylpyridine, m. p.  $72^\circ$ . 3-Benzoylisonicotinic acid at its m. p.,  $270^\circ$ , is changed to 3-benzoylpyridine, b. p.  $307^\circ$ .

C. S.

**Anthranil. XI.** EUGEN BAMBERGER (*Ber.*, 1909, 42, 1647—1676).—Polemical. A reply to Heller (Abstr., 1908, i, 267). C. S.

**Anthranil. XII.** Anthranil and Methylantranil. EUGEN BAMBERGER and JARL LUBLIN (*Ber.*, 1909, 42, 1676—1707. Compare preceding abstract).—Heller claims to support his imide formula for anthranil by the production of a nitrosoamine (Abstr., 1908, i, 267),



sufficiently pure to decide between the two formulæ). The authors show that the nitrosoamine is in reality *o*-aldehydophenylnitrosohydroxylamine,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{NO}) \cdot \text{OH}$ , m. p.  $52.5^\circ$  (decomp.), the chief points in the proof being (1) the acid character of the substance; (2) the striking resemblance between the iron salt, which is soluble in ether, and the iron salt of nitrosophenylhydroxylamine; (3) its decomposition by cold mineral acids, forming a solution of diazo-salts, among which the presence of diazotised *o*-aminobenzaldehyde is detected by the formation of salicylaldehyde by warming, and (4) its conversion into *o*-azoxybenzaldehyde.

*o*-Aldehydophenylnitrosohydroxylamine is obtained by slowly adding very finely powdered and sifted sodium nitrite to a continuously-stirred solution of anthranil in 23% hydrochloric acid at  $-17^\circ$ , washing the resulting crystals with 23% hydrochloric acid at  $-17^\circ$  and with water at  $0^\circ$  (the filtrate contains *o*-aldehyddiazobenzene chloride), drying them on porous tile at  $0^\circ$ , and converting them by alcoholic potassium hydroxide at  $-15^\circ$  into the white, crystalline potassium salt, the aqueous solution of which, when decomposed by metaphosphoric acid, yields pure aldehydophenylnitrosohydroxylamine.

From the potassium salt the *silver, lead, nickel, cobalt, copper, mercury,* and *barium* salts have been obtained. The *p*-nitrophenylhydrazone,  $C_{13}H_{11}O_4N_5$ , has m. p.  $171^\circ$  (decomp.; corr.). An alcoholic solution of *o*-aldehydophenylnitrosohydroxylamine, containing a little water, deposits *o*-azoxybenzaldehyde (Abstr., 1907, i, 163) when kept overnight at  $-10^\circ$ .

With regard to the homology of anthranil and methylantranil, Heller states (*loc. cit.*) that these compounds do not behave alike to hydrochloric acid and sodium nitrite under the same conditions, since anthranil yields the (so-called) nitrosoamine, whereas methylantranil forms methylantranil dichloride (Bamberger and Elger, Abstr., 1903, i, 561). The author points out that the conditions are not the same; he and Elger used 39% hydrochloric acid, whilst Heller used 23% acid. With 39% hydrochloric acid and sodium nitrite at  $-16^\circ$  to  $-18^\circ$ , anthranil behaves like methylantranil, forming a *dichloride*,  $C_7H_5ONCl_2$ , m. p.  $77^\circ$ . Moreover, methylantranil behaves with 23% hydrochloric acid and sodium nitrite at  $-17^\circ$  like anthranil, forming *o*-acetylphenylnitrosohydroxylamine,  $COMe \cdot C_6H_4 \cdot N(NO) \cdot OH$ , and *o*-acetyldiazobenzene chloride. Anthranil and methylantranil are therefore analogously constituted. C. S.

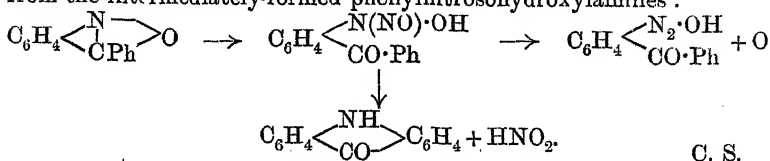
**Anthranil. XIII. Diazotisation of Anthranils and Conversion of Arylanthranils into Acridones.** EUGEN BAMBERGER (*Ber.*, 1909, 42, 1707—1723).—Methylantranil (2-methylbenz- $\psi$ -oxazole),  $C_6H_4 \begin{smallmatrix} \text{CMe} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{O}$ , is converted by nitrous acid into a

diazonium salt of  $\alpha$ -aminoacetophenone (Abstr., 1903, i, 561). Other  $\psi$ -benzoxazoles, such as anthranil and its *Bz*-chlorinated or brominated derivatives (preceding abstract), phenylantranil, *p*-tolylantranil, anthroxanic acid, and its aldehyde behave in a similar manner, as also do thioanthranil and benzoxazole; substituted phenylnitrosohydroxylamines are probably formed as intermediate products (preceding abstract). The process of diazotisation differs somewhat for each substance, but as a rule the substance is dissolved in 62 or 75% sulphuric acid and treated with 10% nitrite at  $0^\circ$  to  $-10^\circ$ , and the resulting solution is added to alkaline  $\alpha$ -naphthol; the red colour usually develops at once, but only after forty-eight hours in the case of benzoxazole, and after ten days in the case of benzthiazole.

The compounds obtained by Zincke by the condensation of *o*-nitrobenzaldehyde and aromatic amines or phenols in the presence of hydrochloric acid may be formulated as  $\psi$ -benzoxazoles (Abstr., 1906, i, 110, 515) or as acridones (Abstr., 1904, i, 530). Since the compounds react with 62% sulphuric acid or 23% hydrochloric acid and 10% sodium nitrite at  $0^\circ$  to form diazonium salts, they are probably  $\psi$ -benzoxazoles; 3-methylacridone is stable to 62% sulphuric acid and sodium nitrite at  $0^\circ$ .

The action of sulphuric acid and sodium nitrite on phenyl- and *p*-tolyl-anthranil yields only a small quantity of the diazonium salt, the chief product being acridone and 3-methylacridone respectively. Since 62% sulphuric acid alone at  $-10^\circ$  does not cause the formation

of the acridone, the latter and the diazonium salt are probably obtained from the intermediately-formed phenylnitrosohydroxylamines :



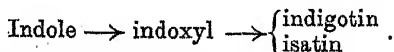
C. S.

**Phenylanthranil (2-Phenyl- $\psi$ -benzoxazole).** EUGEN BAMBERGER and SVEN LINDBERG (*Ber.*, 1909, 42, 1723—1725).—Phenylanthranil is obtained by the oxidation of *o*-aminobenzophenone by Caro's acid, or, better, by the reduction of *o*-nitrobenzophenone by tin and hot glacial acetic acid. It has m. p. 52—53°, is volatile with steam, and yields acridone when strongly heated (compare Kliegl, this vol., i, 255).

C. S.

**Researches on Indole. I. Action of Oxidising Agents.** CH. PORCHER (*Bull. Soc. chim.*, 1909, [iv], 5, 526—540).—It is shown that whereas indole is oxidised by hydrogen peroxide, yielding indoxyl and oxidation products of this, the action of ammonium persulphate and of quinone is quite different. The action of hydrogen peroxide is probably akin to that which goes on in the organism.

When indole is added to an aqueous solution of hydrogen peroxide, the latter quickly becomes yellowish-green, and indigotin begins to separate after some hours. On shaking the filtrate with amyl alcohol, indoxyl is dissolved out, and is recognised by its oxidation to indigotin on shaking with alkali, or its conversion into indirubin in presence of isatin and hydrochloric acid. This latter test is delicate, and can be used for the detection of indoxyl free, or in the form of its derivatives. It is always necessary in applying the test to mixtures to separate the indoxyl first by extraction with chloroform or ether. The oxidation of indole by hydrogen peroxide goes on more rapidly at 100°, and under these conditions the reaction appears to take place according to the scheme :



There is also formed some indirubin, which, however, disappears if the oxidation is prolonged. Isatin was detected by the indophenine reaction, and indigo-red was separated from indigotin by extraction with ether. The oxidation of indole to indoxyl, and eventually indigotin, can be used for the detection of this substance in presence of its homologues, such as scatole.

The chief product of the action of ammonium persulphate on indole in water at 100° is a black, flocculent precipitate, and neither indoxyl nor indigotin could be detected, although under certain conditions isatin was formed and possibly indirubin. With quinone in solution, in ether, and in presence of light, indole gives some indirubin, but not indigotin. Details of the methods of applying the various tests used for the detection of the oxidation products are given in the original.

T. A. H.

**Iodo-2-methylindole.** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, 60, 289—291. Compare Rhode, *ibid.*, 1905, 44, 161; Neuberg, Abstr., 1907, i, 995).—A crystalline *iodo-2-methylindole*,  $C_9H_8NI$ , can be prepared by adding finely divided iodine to a mixture of sodium hydrogen carbonate and an alcoholic solution of 2-methylindole.

It forms pale brownish-violet plates, m. p.  $82^\circ$ , decomposes when exposed to light, and the addition of nitrous acid liberates iodine.

J. J. S.

**Perhydrogenated Quinolines.** HERMANN FINGER and W. BREITWIESER (*J. pr. Chem.*, 1909, [ii], 79, 454—456).—3-Cyano-6-methylquinoline when reduced with sodium and alcohol yields 6-methyldecahydroquinoline, although 6-methylquinoline when similarly treated does not yield the decahydro-derivative.

3-Cyano-6-methylquinoline,  $C_{11}H_8N_2$ , prepared by diazotising 3-amino-6-methylquinoline (compare Noetting and Trautmann, Abstr., 1891, 325) and treating the diazo-compound with potassium cuprous cyanide, forms small, colourless crystals, m. p.  $104-105^\circ$ ; all attempts to hydrolyse it to the corresponding acid have been unsuccessful.

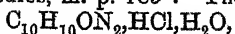
6-Methyldecahydroquinoline, prepared in the manner described or by reducing 6-methyltetrahydroquinoline with hydriodic acid and phosphorus, is a colourless, crystalline substance, m. p.  $44^\circ$ , b. p.  $222-225^\circ/750$  mm.; the *hydrochloride*,  $C_{10}H_{16}N.HCl$ , was analysed. The base interacts with phenylcarbimide, yielding the corresponding *thiocarbamide* derivative,  $C_{17}H_{24}N_2S$ , a crystalline substance, m. p.  $138^\circ$ .

W. H. G.

**Amino- and Hydroxy-quinolones.** HERMAN DECKER and HARRY ENGLER (*Ber.*, 1909, 42, 1736—1742. Compare Abstr., 1903, i, 719).—5-Amino-1-methyl-2-quinolone,  $C_9NH_5.OMe.NH_2$ , obtained by reducing the corresponding nitro-compound (Abstr., 1901, i, 654) with an aqueous solution of ammonium sulphide, separates from benzene in pale yellow crystals, m. p.  $213^\circ$ . The *hydrochloride*,  $C_{10}H_{10}ON_2.HCl$ , crystallises in clear yellow needles, m. p.  $221^\circ$  and the *acetyl* derivative,  $C_{12}H_{12}O_2N_2.H_2O$ , crystallises from water in yellow needles, m. p.  $237^\circ$ . 5-Amino-1-ethyl-2-quinolone,  $C_{11}H_{12}ON_2$ , obtained in a similar manner from 5-nitro-1-ethylquinolone, crystallises in small, glistening plates, m. p.  $177-178^\circ$ . The crystals obtained from its aqueous solutions contain  $1H_2O$ . The *hydrochloride* crystallises from water in glistening, pale yellow needles containing  $2H_2O$ . It loses the water of hydration at  $120^\circ$ , and then melts and decomposes at  $235^\circ$ .

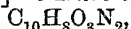
8-Amino-1-methylquinolone is somewhat less soluble in water or alcohol than the isomeric-6-amino-compound, and separates from benzene in small, glistening, yellow crystals, m. p.  $180^\circ$ . The *formyl* derivative crystallises from dilute alcohol in colourless needles, m. p.  $88^\circ$ , containing water of crystallisation. The *acetyl* derivative has m. p.  $174^\circ$ .

7-Amino-1-methyl-2-quinolone is less soluble than its isomerides, crystallises with  $H_2O$ , which it loses in a desiccator, and sublimes in colourless, glistening needles, m. p.  $185^\circ$ . The *hydrochloride*,

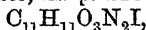


forms golden-yellow needles, which lose their  $\text{H}_2\text{O}$  at  $110-120^\circ$  and then melt and decompose at  $244^\circ$ . The *acetyl* derivative,  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_2$ , crystallises from benzene in glistening prisms, m. p.  $211^\circ$ .

[With WLADIMIR RUMINE.]—5-Nitro-6-methoxyquinoline,



obtained by nitrating *p*-methoxyquinoline, crystallises from alcohol in orange-yellow needles, m. p.  $104-105^\circ$ . The *nitrate* forms colourless crystals, m. p.  $195^\circ$ ; the *hydrochloride* has m. p.  $219^\circ$ ; the *sulphate*, m. p.  $205^\circ$ ; the *chromate* forms a brown precipitate, m. p.  $162^\circ$ , and the *picrate*, a yellow precipitate, m. p.  $211^\circ$ . The *methiodide*,



has m. p.  $275^\circ$ , and yields a *picrate*, which crystallises in yellow needles, m. p.  $168^\circ$ , and a *chromate*, as orange-coloured plates, which decompose at  $160^\circ$ . The methyl sulphate derivative is readily soluble, and when oxidised with potassium ferricyanide yields 5-nitro-6-methoxy-1-methyl-2-quinolone,  $\text{OMe}\cdot\text{C}_9\text{NH}_4\text{MeO}\cdot\text{NO}_2$ , which has m. p.  $194^\circ$  and sublimes at  $198^\circ$ .

J. J. S.

#### A New Synthesis of Dihydroisoquinoline Derivatives.

HERMAN DECKER and WALTER KROPP (*Ber.*, 1909, 42, 2075—2078).

—The formation of 3:4-dihydroisoquinoline derivatives from  $\beta$ -phenylethylamine by loss of water (Bischler and Napieralski, *Abstr.*, 1893, i, 608) is of importance as leading to compounds closely related to the opium and other alkaloids. The reaction only takes place at a high temperature, and fails in certain cases. It is now found that the condensation proceeds regularly below  $100^\circ$  in presence of aluminium chloride.

1-Phenyl-3:4-dihydroisoquinoline,  $\text{C}_{15}\text{H}_{13}\text{N}$ , prepared by warming benzoylphenylethylamine with phosphorus pentachloride, removing the phosphoryl chloride by distillation, warming the residue with light petroleum and aluminium chloride, and purifying by extracting the alkaline solution with ether, forms an oil, b. p.  $194-196^\circ/23$  mm. (corr.). The platinichloride,  $(\text{C}_{15}\text{H}_{13}\text{N})_2\text{H}_2\text{PtCl}_6$ , has m. p.  $230-233^\circ$  when quickly heated (compare Bischler and Napieralski, *loc. cit.*); the *picrate* forms flat, yellow, rhombic needles, m. p.  $175^\circ$ .

Phenylacetyl- $\beta$ -phenylethylamine,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , prepared from  $\beta$ -phenylethylamine, crystallises from aqueous alcohol in plates, m. p.  $94-95^\circ$ .

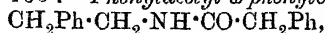
$\beta$ -Phenylethylamine *picrate* has m. p.  $171^\circ$  (corr.) (compare Michaelis, Schroeter, and Linow, *Abstr.*, 1893, i, 703).

C. H. D.

Synthesis of *iso*Quinoline Bases. AMÉ PICTET and FRANCIS W. KAY (*Ber.*, 1909, 42, 1973—1979).—Since the majority of the opium alkaloids are derived from 1-benzylisoquinoline, a simple method for the synthesis of this and similar bases is desirable. Many investigators have achieved partial success; the authors find that a modification of Bischler and Napieralski's method (*Abstr.*, 1893, i, 608) gives the desired result. Acyl- $\omega$ -phenylethylamines,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$ , and phosphoric oxide are heated in boiling benzene, toluene, or xylene, the selection of the solvent being determined by the particular acyl compound under examination. The

constitution of the resulting dihydroisoquinoline base is determined by its oxidation to the corresponding isoquinoline by acidified potassium permanganate.

1-Phenyl-3:4-dihydroisoquinoline,  $C_{15}H_{13}N$ , m. p. 73—74°, b. p. 320°/718 mm., prepared from benzoyl- $\omega$ -phenylethylamine, forms a hydrochloride, m. p. 222—223°, platini-chloride, m. p. 229—230° (decomp.), and a picrate, m. p. 163°. 1-Methyl-3:4-dihydroisoquinoline forms a hydrochloride, m. p. 160°, a nearly colourless platini-chloride, m. p. 223°, picrate, m. p. 188—190°, and a dichromate, which decomposes at 150—160°. Phenylacetyl- $\omega$ -phenylethylamine,



m. p. 95°, is obtained by shaking equal molecular quantities of  $\omega$ -phenylethylamine and phenylacetyl chloride with 20% sodium hydroxide below 0°. When heated with phosphoric oxide in boiling xylene, it yields 1-benzyl-3:4-dihydroisoquinoline,  $C_{16}H_{15}N$ , b. p. 300° (decomp.), or 196—197°/12 mm. (picrate, m. p. 174—175°; platini-chloride, m. p. 197°, decomp.), which is oxidised to 1-benzylisoquinoline by potassium permanganate and glacial acetic acid. C. S.

**Another Case of Stereoisomerism of Compounds containing Asymmetric Nitrogen and Active Asymmetric Carbon.** EDGAR WEDEKIND and F. NEY (*Ber.*, 1909, 42, 2138—2142).—The fractional crystallisation of the product of the interaction of 2-propyl-tetrahydroisoquinoline with *l*-menthyl iodoacetate has yielded two stereoisomeric salts of the annexed formula, which have  $[\alpha]_D - 31.7^\circ$  and  $-23.2^\circ$ , and contain a laevo-rotatory and dextrorotatory ammonium complex respectively, as

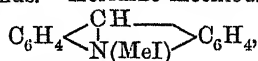
shown by the fact that, on treatment with silver oxide in methyl-alcoholic solution, they yield different betaines, one of which is dextro-, and the other laevo-rotatory.

isoquinoline propiodide, obtained by mixing isoquinoline with propyl iodide, separates from alcohol in yellow crystals, m. p. 115—118°; on reduction with tin and hydrochloric acid it is converted into 2-propyltetrahydroisoquinoline, a light yellow oil, b. p. 259—260°/743 mm.

The latter substance, when gently warmed with *l*-menthyl iodoacetate, yields a glassy, viscous substance, which, on crystallisation from acetone, gives glistening needles of menthyl 2-propyltetrahydroisoquinolinium-iodide-*l*-acetate,  $C_{24}H_{38}O_2NI$ , m. p. 189° (decomp.); the mother liquors contain a more soluble isomeric variety, m. p. 169° (decomp.); the less fusible substance has  $[\alpha]_D - 23.2^\circ$ , and the more fusible one,  $[\alpha]_D - 31.7^\circ$ . The betaines obtained from these two substances very rapidly became inactive, and were too unstable to be examined more closely. P. H.

**Action of Grignard's Solutions on Halogen Ammonium Compounds.** MARTIN FREUND and GEORG BODE (*Ber.*, 1909, 42, 1746—1766. Compare Abstr., 1906, i, 600; this vol., i, 417).—Organic ammonium compounds which yield pseudo-bases under the

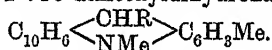
influence of alkalis react with Grignard's compounds in such a manner that the hydroxyl of the  $\psi$ -base is replaced by an alkyl group. This generalisation is illustrated in the case of various acridinium and isoquinolinium compounds. Acridine methiodide,



yields a  $\psi$ -base,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C}_6\text{H}_4$ , and with organo-magnesium compounds yields alkyl derivatives of 10-methyldihydroacridine,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CHR} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C}_6\text{H}_4$ . The following compounds have been prepared from acridine methiodide by this method: 9-Phenyl-10-methyldihydroacridine (Bernthsen and Bender, Abstr., 1883, 1134); 9-benzyl-10-methyldihydroacridine,  $\text{C}_{21}\text{H}_{19}\text{N}$ , colourless needles, m. p. 108°, which reacts with an alcoholic solution of iodine, yielding a black periodide, and from this sulphurous acid liberates benzylacridine methiodide (Decker and Hock, Abstr., 1904, i, 620); 10-methyl-9-ethyldihydroacridine,  $\text{C}_{16}\text{H}_{17}\text{N}$ , colourless needles, which turn yellowish-brown on exposure to the air, m. p. 70–73°; 9:10-dimethyldihydroacridine,  $\text{C}_{15}\text{H}_{15}\text{N}$ , colourless, pearly plates, m. p. 135–140°; 10-methyl-9-isopropyldihydroacridine,  $\text{C}_{17}\text{H}_{19}\text{N}$ , colourless needles, m. p. 99–102°.

10-Methyl-9-diethyl- $\psi$ -hydroacridine,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CEt}_2 \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C}_6\text{H}_4$ , is formed by the action of ethyl magnesium bromide on ethylacridine methiodide. It crystallises from alcohol in colourless prisms, m. p. 80–85°.

Grignard compounds also react with the methiodide of 2'-methyl-1:2-naphthacridine (Ullmann and Naef, Abstr., 1900, i, 360), yielding derivatives of 2':10-dimethyldihydronaphthacridine,



2':9:10-Trimethyldihydronaphthacridine,  $\text{C}_{20}\text{H}_{19}\text{N}$ , crystallises from alcohol in colourless plates, m. p. 150–160°; 2':10-dimethyl-9-ethyldihydronaphthacridine,  $\text{C}_{21}\text{H}_{21}\text{N}$ , forms colourless needles, m. p. 132°, after sintering at 125°; 9-phenyl-2':10-dimethyldihydronaphthacridine,  $\text{C}_{25}\text{H}_{21}\text{N}$ , crystallises from ethyl acetate in colourless needles, m. p. 187–191°, and the corresponding 9-benzyl derivative,  $\text{C}_{26}\text{H}_{23}\text{N}$ , crystallises from alcohol in colourless needles, m. p. 145°. The substituted dihydroacridines do not possess basic properties. The product obtained by the action of magnesium on an ethereal solution of ethylene bromide does not react with acridine methiodide (compare Abstr., 1906, i, 602). The methiodide of diacetylbenzoflavin (Hewitt and Fox, Trans., 1905, 87, 1058) does not react with Grignard reagents.

isoQuinoline methiodide,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH:CH} \\ \diagup \quad \diagdown \\ \text{CH:NMeI} \end{array}$ , reacts with Grignard compounds, yielding 1-alkyl derivatives of 2-methyl-1:2-dihydroisoquinoline,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH=CH} \\ \diagup \quad \diagdown \\ \text{CHR:NMe} \end{array}$ . 1:2-Dimethyl-1:2-dihydroisoquinoline,  $\text{C}_{11}\text{H}_{13}\text{N}$ , has b. p. 150°/20 mm.; the *platinichloride*,  $(\text{C}_{11}\text{H}_{13}\text{N})_2\text{H}_2\text{PtCl}_6$ ,

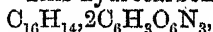
sinters at  $160^{\circ}$  and decomposes at  $167^{\circ}$ . When the base is reduced with sodium and alcohol it yields 1:2-dimethyltetrahydroisoquinoline,  $C_{11}H_{15}N$ , as a colourless liquid, b. p.  $121-125^{\circ}/20$  mm.; the corresponding methiodide,  $C_{13}H_{18}NI$ , crystallises from alcohol in plates.

2-Methyl-1-ethyl-1:2-dihydroisoquinoline,  $C_{15}H_{19}N$ , has b. p.  $165^{\circ}/45$  mm., and when reduced with tin and hydrochloric acid yields the tetrahydro-base,  $C_{15}H_{17}N$ , as an oil, b. p.  $135^{\circ}/30$  mm.; the methiodide,  $C_{18}H_{20}NI$ , of the latter crystallises in prisms, sinters at  $158^{\circ}$ , and decomposes at  $159-160^{\circ}$ .

1-Phenyl-2-methyl-1:2-dihydroisoquinoline,  $C_{16}H_{15}N$ , has b. p.  $220^{\circ}/30$  mm., and crystallises from alcohol in colourless needles, m. p.  $55-60^{\circ}$ . The platinichloride has m. p.  $158^{\circ}$  (decomp.).

1-Phenyl-2-methyltetrahydroisoquinoline,  $C_{16}H_{17}N \cdot H_2O$ , crystallises from dilute alcohol in colourless needles, m. p.  $120-130^{\circ}$ , after sintering at  $65-70^{\circ}$ . The methiodide,  $C_{17}H_{20}NI$ , forms colourless prisms, m. p.  $240-243^{\circ}$ . 1-Benzyl-2-methyl-1:2-dihydroisoquinoline,  $C_{17}H_{17}N$ , has b. p.  $170-180^{\circ}/9$  mm., and the platinichloride has m. p.  $150-155^{\circ}$ . The corresponding tetrahydro-base,  $C_{17}H_{19}N$ , has b. p.  $177-180^{\circ}/12$  mm., and yields a platinichloride, which crystallises in orange-red plates, m. p.  $200^{\circ}$ . The picrate forms rhombic plates, m. p.  $165-166^{\circ}$ ; the hydriodide, prisms, m. p.  $175-180^{\circ}$ , and the methiodide,  $C_{18}H_{22}NI$ , prisms, m. p.  $239-242^{\circ}$ .

When the methiodide of 1-benzyl-2-methyltetrahydroisoquinoline is treated with silver oxide in the presence of dilute alcohol and then with concentrated sodium hydroxide solution, it yields o-dimethylaminoethylstilbene,  $CHPh \cdot CH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_2$ . The hydrochloride,  $C_{18}H_{21}N \cdot HCl$ , crystallises from dilute alcohol in colourless prisms, m. p.  $105-110^{\circ}$ , containing  $1H_2O$ . When dried at  $110^{\circ}$  it has m. p.  $160-165^{\circ}$ . The hydriodide has m. p.  $160-167^{\circ}$ , and the methiodide,  $C_{19}H_{24}NI$ , m. p.  $175-185^{\circ}$ . When the methiodide is heated with aqueous-alcoholic sodium hydroxide, it yields o-vinylstilbene,  $C_{16}H_{14}$ , as an oil. This hydrocarbon forms a picrate,



which crystallises from dilute alcohol in orange-red needles, m. p.  $95-100^{\circ}$ , and a tetrabromide,  $CH_2Br \cdot CHBr \cdot C_6H_4 \cdot CHBr \cdot CHBrPh$ , which crystallises from glacial acetic acid in colourless plates, m. p.  $165-168^{\circ}$ .

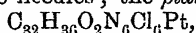
The derivatives of 1:2-dihydroisoquinoline are much less stable than derivatives of 3:4-dihydroisoquinoline (cotarnine derivatives).

Definite products have not been obtained by the action of Grignard compounds on dinaphthazine methiodide, m-tolyiminazole methiodide, or pyridine methiodide.

J. J. S.

**Behaviour of Hydroxy-p-phenylenediamine and its Unsymmetrical Dialkyl Derivatives in Acetic Acid Solution on Oxidation with Air.** FRIEDRICH KEHRMANN and W. POPLAWSKI (*Ber.*, 1909, 42, 1275-1278).—A warm aqueous solution of o-hydroxy-p-phenylenediamine hydrochloride and sodium acetate gives, on passing air through it, a small quantity of 3:9-diaminophenoxazonium chloride (*Abstr.*, 1903, i, 280). This result confirms the constitution previously assigned to the substance. A 50% yield of 3:9-tetramethyldiamino-

*phenoxazonium nitrate*,  $C_{10}H_{18}O_4N_4 \cdot H_2O$ , is obtained by the oxidation of a similar solution of *o*-hydroxy-*as*-dimethyl-*p*-phenylenediamine; it forms long, green, metallic needles; the *platinichloride*,

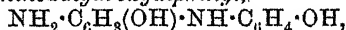


is a dark blue, microcrystalline powder. The unsymmetrical hydroxy-dimethyl-*p*-tolylene-diamine also gives a dye of the Capri-series under like conditions.

W. R.

**Quinonoid Compounds. XVIII. *meri*-Quinoneimines. III.**  
 RICHARD WILLSTÄTTER and JEAN PICCARD (*Ber.*, 1909, 42, 1902—1907. Compare Abstr., 1908, i, 475, 915).—It has been found possible to isolate the violet dye obtained by the oxidation of *p*-aminophenol with cold ferric chloride solution. It has the composition  $C_{12}H_{10}O_2N_2 \cdot HCl$ , and may be crystallised from dilute acid provided precautions are taken. It forms brilliant, opaque prisms with a coppery lustre, and may also be obtained in a pure state by oxidising its leuco-compound with ferric chloride in 2*N*-hydrogen chloride solution. Its solutions have a violet colour, and are not decolorised by the addition of much water or of acid. The dye does not yield quinone with acids, and when oxidised with dichromate only one-half of the molecule is converted into benzoquinone. The dye thus appears to be a condensation product of anilinoquinone constitution.

The *leuco-base*, *aminodihydroxydiphenyl*,



obtained by reducing the dye with stannous chloride, yields a *hydrochloride*,  $C_{12}H_{12}O_2N_2 \cdot 2HCl$ , in the form of prisms sparingly soluble in alcohol. The *basic chloride*,  $C_{12}H_{13}O_2N_2 \cdot HCl$ , is readily soluble in alcohol. The base forms crystalline aggregates, m. p. 202—203°, and its alkaline solutions readily turn red.

J. J. S.

**Compounds of Benzidine with Sugars, and a Method for Removing Dextrose from Mixtures of Dextrose and Lævulose.** OSCAR ADLER (*Ber.*, 1909, 42, 1742—1746).—Alcoholic solutions of benzidine react with sugars, yielding crystalline compounds analogous to compounds of sugars with aniline and toluidine (Sorokin, Abstr., 1887, 526, 683). They form light crystalline powders, insoluble in ether, but soluble in hot alcohol or water. Their solutions react in much the same manner as their components.

A crystalline compound with lævulose could not be isolated, even when the solutions were evaporated to syrupy consistency. When an alcoholic solution containing both dextrose and lævulose is mixed with benzidine and concentrated by evaporation, the greater part of the dextrose can be removed in the form of the crystalline benzidine derivative, and the mother liquors are then much richer in lævulose.

*Didextrose benzidide*,  $C_{24}H_{34}O_{10}N_2$ , crystallises from 96% alcohol in colourless, microscopic needles, m. p. 127° (decomp.). Its alcoholic solution is strongly laevorotatory, and it can be fermented by yeast. *Diarabinose benzidide*,  $C_{22}H_{28}O_8N_2$ , forms a pale yellow, microcrystalline powder, m. p. 86° (decomp.), and its solution in 50% alcohol is inactive. *Dimaltose benzidide*,  $C_{36}H_{52}O_{20}N_2$ , is a colourless, microcrystalline

powder, m. p. 175°, after previous sintering. Its aqueous solution is dextrorotatory, and exhibits mutarotation. J. J. S.

**Nucleus-substituted Triphenylmethane Dyes.** HERMANN FINGER (*J. pr. Chem.*, 1909, [ii], 79, 492—497).—An account of the preparation and properties of trichloro- and trimethoxy-magenta. The introduction of the chlorine into the magenta benzene nuclei results in the production of lighter shades of colour in dyeing, whilst the methoxy-groups produce a deepening effect towards violet.

3:3'-Dichloro-4:4'-diaminodiphenylmethane,  $C_{13}H_{15}N_2Cl_2$ , prepared by boiling methylenedi-*o*-chloroaniline, m. p. 74° (Bischoff and Reinfeld, *Abstr.*, 1903, i, 247, give m. p. 84°), with *o*-chloroaniline and *o*-chloroaniline hydrochloride in alcohol, is a crystalline substance; m. p. 105°; the dihydrochloride, m. p. 201°, is very unstable.

The colour base obtained by heating 3:3'-dichloro-4:4'-diaminodiphenylmethane with *o*-chloroaniline, *o*-chloroaniline hydrochloride, and arsenic acid, could not be obtained in a colourless or crystalline condition; the hydrochloride is a dark red powder with a metallic green reflex; the picrate was prepared and analysed.

4:4'-Diamino-3:3'-dimethoxydiphenylmethane,  $C_{15}H_{18}O_2N_2$ , prepared from methylenedi-*o*-anisidine, is a crystalline substance, m. p. 100°; the diacetyl derivative,  $C_{19}H_{22}O_4N_2$ , crystallises in nodules, m. p. 180·5°, and when oxidised with chromic acid yields diacetyldiaminodimethoxybenzophenone,  $C_{19}H_{20}O_5N_2$ , crystallising in pale yellow leaflets, m. p. 208—209°. 4:4'-Diamino-3:3'-dimethoxybenzophenone,

$C_{15}H_{18}O_3N_2$ , forms small, pale yellow crystals, m. p. 227°, and when reduced yields 4:4'-diamino-3:3'-dimethoxybenzhydrol, obtained as a fine yellow powder, m. p. 160°. Trimethoxymagenta,  $C_{23}H_{24}O_3N_2Cl$ , prepared from 4:4'-diamino-3:3'-dimethoxydiphenylmethane by heating with *o*-anisidine hydrochloride, *o*-nitroanisole, and a small quantity of ferric chloride at 180°, is obtained as coppery-red granules with a green reflex; the colour base is almost black. W. H. G.

**New Kind of Isomerism in the Hydroxy- and Alkoxy-Malachite-Green Series.** EMIL VOTOČEK and OTTIL KRAUZ (*Ber.*, 1909, 42, 1602—1611. Compare *Abstr.*, 1907, i, 245).—In a few cases the condensation previously investigated of hydroxy- and alkoxy-aldehydes with dimethylaniline proceeded abnormally, and a more accurate study of these interactions has now been made. The condensation of  $\beta$ -naphthaldehyde and dimethylaniline in alcoholic hydrogen chloride at 120° for twenty hours gave the leuco-base of methyl-violet (hexamethyltriaminotriphenylmethane). This abnormal result is shown to be due to the aldehyde on heating liberating formic acid, which then condenses with the dimethylaniline to form tetramethyldiaminobenzhydrol, and this in its turn yields the leuco-base with more of the aniline. The leuco-base from protocatechualdehyde is dihydroxytetramethyldiaminotriphenylmethane (compare *Abstr.*, 1897, i, 157), identical with that obtained from the hydrol and catechol. Resorcinolaldehyde in a similar manner gives a dihydroxytetramethyldiaminotriphenylmethane,  $C_{23}H_{26}O_2N_2$ , m. p. 204—205°, and when

oxidised gives a dirty blue dye; pyrogallaldehyde, a *trihydroxytetramethyldiaminotriphenylmethane*,  $C_{24}H_{26}O_3N_2$ , of m. p.  $170-172^\circ$ , which oxidises to a dirty blue dye.

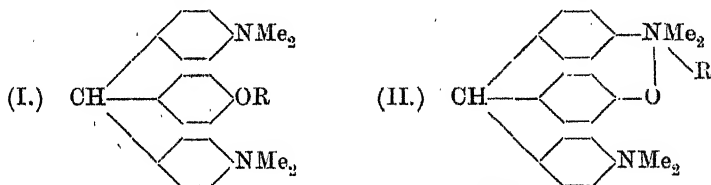
The leuco-base obtained from gentisinaldehyde and dimethylaniline is not identical with that from the hydrol-quinol condensation, although this would be expected to give the same compound if, as is usual, the para-positions to the amino-groups were those affected in the change. The base is a *dihydroxytetramethyldiaminotriphenylmethane*,  $C_{23}H_{26}O_2N_2$ , of m. p.  $165^\circ$ ; the corresponding dye is blue.

In order further to elucidate the differences existing in these compounds, the methoxymalachite-greens have been studied. *o*-Methoxybenzaldehyde gives with dimethylaniline a *methoxyleucomalachite-green*,  $C_{24}H_{28}ON_2$ , of m. p.  $155^\circ$ , which, although identical in m. p. and composition with that formerly obtained from anisole and tetramethyldiaminobenzhydrol (1907, *loc. cit.*), is yet a different substance, giving a mixed m. p. of  $118^\circ$  and a dye stable towards alkalis. Likewise, the leuco-bases from *m*- and *p*-methoxybenzaldehydes are different from the hydrol compound. The leuco-base from the hydrol-phenol condensation on methylation by means of methyl sulphate in a closed tube at  $100^\circ$  for four hours gives the same leuco-base as is obtained from anisole. There are therefore four methoxy-leuco-bases obtained, and only three theoretically possible.

The *ethoxyleucomalachite-greens*,  $C_{25}H_{30}ON_2$ , from *o*-, *m*-, and *p*-ethoxybenzaldehyde have m. p.'s  $119^\circ$ ,  $120^\circ$ , and  $125^\circ$  respectively, whereas that formerly obtained from phenetole, as well as the methylation of the phenol leuco-base, has m. p.  $165^\circ$ .

The dye from the anisaldehyde-dimethylaniline condensation on hydrolysis with hydrochloric acid in a closed tube at  $140^\circ$  gave methyl chloride, phenol, and 4:4'-tetramethyldiaminobenzophenone (Michler's ketone), and similar results were obtained with the dyes from *o*- and *m*-hydroxybenzaldehydes. The conclusion is drawn that in these condensations both the amino-groups are in the para-positions.

The suggestion is made that one series of the leuco-bases is normal, and in the other they have a betaine-like structure, thus:



that from the hydrol having the structure (II). It is further shown that the leuco-base from anisaldehyde is transformed into the leuco-base from the hydrol by heating with hydrochloric acid in a sealed tube at  $120^\circ$  for one hour, but the reverse change with sodium hydroxide did not take place.

W. R.

**Hydrazones of Sugars and their Acetates.** ADOLF HOFMANN (*Annalen*, 1909, 366, 277—323).—With the object of gaining some knowledge as to the nature of the isomerism of the dextrosephenyl-

hydrazones described by Behrend and Lohr (Abstr., 1908, i, 765), attempts have been made to prepare isomeric phenylhydrazones of various sugars. Although mixtures of isomerides were obtained, it was not found possible in any case to isolate both forms. Noteworthy is the fact that *p*-bromophenylhydrazine reacts with lævulose in alcoholic solution only in the presence of acetic acid, whilst it does not appear to condense with lactose under any conditions; further,  $\alpha$ -phenylbenzylhydrazine interacts with lactose only in the presence of acetic acid, whilst maltose does not yield an  $\alpha$ -phenylbenzylhydrazone.

Attempts were also made to isolate the second isomeride of the phenylhydrazones exhibiting mutarotation, by conversion into acetates. The solution of the hydrazone in pyridine, after attaining a state of equilibrium, was treated with acetic anhydride, but in no case was even a mixture of isomerides obtained. The acetates prepared in this manner are probably penta-acetates; the imino-hydrogen atom of the hydrazone is apparently not replaced by acetyl, since benzaldehydephenylhydrazone is not acetylated in pyridine solution.

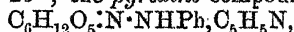
Dextrose- $\alpha$ -phenylhydrazone and - $\beta$ -phenylhydrazone yield isomeric acetates, neither of which exhibits mutarotation, from which observation the conclusion is drawn that one of the dextrosephenylhydrazones is a true hydrazone, whilst the other is a hydrazide (compare Behrend and Lohr, *loc. cit.*).

*Dextrose- $\alpha$ -phenylhydrazone acetate*,  $C_{22}H_{28}H_{10}N_2$  or  $C_{24}H_{30}O_{11}N_2$ , crystallises in long, white needles, sinters at  $150^\circ$ , m. p.  $152-153^\circ$ ,  $[\alpha]_D + 11.97^\circ$  (in pyridine); the corresponding  *$\beta$ -phenylhydrazone acetate* is an amorphous substance, sinters at  $40^\circ$ , m. p.  $50-70^\circ$  (decomp.),  $[\alpha]_D + 100.15^\circ$  to  $+101.34^\circ$ .

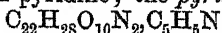
*Dextrose-*p*-bromophenylhydrazone*,  $C_{13}H_{17}O_5N_2Br$ , crystallises in long, thin prisms, sinters at  $146^\circ$ , m. p.  $164-166^\circ$  (decomp.); the solution in pyridine has an initial value,  $[\alpha]_D - 43.67^\circ$ , and final value,  $[\alpha]_D + 18.94^\circ$ . *Dextrose- $\alpha$ -phenylbenzylhydrazone* in pyridine has an initial value,  $[\alpha]_D - 46.33^\circ$ , and final value,  $[\alpha]_D - 48.16^\circ$ ; the *penta-acetate*,  $C_{29}H_{34}O_{10}N_2$ , is an amorphous, pale yellow mass, sinters at  $40^\circ$ , m. p.  $60-80^\circ$ ,  $[\alpha]_D + 112.48^\circ$  (in pyridine).

*Mannosephenylhydrazone* does not exhibit mutarotation; the *acetate*,  $C_{25}H_{28}O_{10}N_2$  or  $C_{24}H_{30}O_{11}N_2$ , is an amorphous, reddish-brown mass, sinters at  $40^\circ$ , m. p.  $60-70^\circ$ .

*Galactosephenylhydrazone* in pyridine, ten minutes after dissolution, has the value  $[\alpha]_D + 20.54^\circ$  to  $+20.70^\circ$ ; the final value is  $[\alpha]_D + 9.34^\circ$  to  $+9.23^\circ$ ; the *pyridine* compound,



crystallises in snow-white leaflets, sinters at  $153^\circ$ , m. p.  $156-158^\circ$  (decomp.),  $[\alpha]_D + 17.39^\circ$  (initial value),  $+7.99^\circ$  (final value), in pyridine; the *acetate*,  $C_{22}H_{28}O_{10}N_2$  or  $C_{24}H_{30}O_{11}N_2$ , crystallises in colourless leaflets, m. p.  $131-133^\circ$ ,  $[\alpha]_D$  about  $+44^\circ$  (initial value), about  $42^\circ$  (final value), in pyridine; the *pyridine* compound,



or  $C_{24}H_{30}O_{11}N_2 \cdot C_6H_5N$ , forms white leaflets, sinters at  $103^\circ$ , m. p.  $108-110^\circ$ ,  $[\alpha]_D$  about  $+38^\circ$  (initial value), about  $37^\circ$  (final value).

*Galactose-*p*-bromophenylhydrazone*,  $C_{12}H_{17}O_5N_2Br$ , crystallises in long;

thin needles, sinters at  $164^{\circ}$ , m. p.  $166-167^{\circ}$  (decomp.). The corresponding  $\alpha$ -phenylbenzylhydrazone has the value  $[\alpha]_D -14.26^{\circ}$  in pyridine, and does not exhibit mutarotation; the *pyridine* compound,  $C_6H_{12}O_5 \cdot N \cdot NPh \cdot CH_2Ph \cdot C_5H_5N$ , forms crystals, which sinter at  $106^{\circ}$ , m. p.  $110-112^{\circ}$ ,  $[\alpha]_D -11.35^{\circ}$  (in pyridine); the *pentaacetate*,  $C_{29}H_{34}O_{10}N_2$ , crystallises in short, colourless prisms, sinters at  $125^{\circ}$ , m. p.  $128-130^{\circ}$ ,  $[\alpha]_D +93.21^{\circ}$  (in pyridine); the *pyridine* derivative,  $C_{29}H_{34}O_{10}N_2 \cdot C_5H_5N$ , forms snow-white leaflets, m. p.  $105-110^{\circ}$ ,  $[\alpha]_D +81.85^{\circ}$ .

Attempts to prepare a phenylhydrazone of lævulose were unsuccessful; the *phenylhydrazine* compound,  $C_6H_{12}O_5 \cdot N \cdot NPh \cdot NPh \cdot NH_2$ , crystallises in long, pale yellow needles and prisms, sinters at  $50-60^{\circ}$ , m. p.  $140-150^{\circ}$  (decomp.); the initial values of  $[\alpha]_D$  in alcohol and pyridine are  $+6.37^{\circ}$  and  $+8.30^{\circ}$  respectively, whilst the final values are  $-3.27^{\circ}$  and  $+3.44^{\circ}$  respectively; the *pyridine* compound,  $C_6H_{12}O_5 \cdot N \cdot NPh \cdot C_5H_5N$ , forms small, white plates, sinters at  $96^{\circ}$ , m. p.  $98-100^{\circ}$  (decomp.),  $[\alpha]_D +8.61^{\circ}$  (initial value),  $+3.36^{\circ}$  (final value), in pyridine; the *acetate*,  $C_{22}H_{28}O_{10}N_2$  or  $C_{24}H_{30}O_{11}N_2$ , is a coloured, amorphous mass. Lævulose yields with *p*-bromophenylhydrazine in alcohol containing acetic acid a thick jelly, from which a simple substance could not be isolated.

*Maltose-phenylhydrazone* and *p*-bromophenylhydrazone could be obtained only as syrups.

Lactose- $\alpha$ -phenylbenzylhydrazone sinters at  $162^{\circ}$ , and decomposes at  $164-166^{\circ}$  (compare Lobry de Bruyn and van Eckenstein, Abstr., 1907, i, 41); the solution in pyridine,  $[\alpha]_D -34.7^{\circ}$  to  $-36.1^{\circ}$ , does not exhibit mutarotation; the *octa-acetate*,  $C_{41}H_{50}O_{18}N_2$ , is an amorphous substance, sinters at  $50^{\circ}$ , m. p.  $60-80^{\circ}$  (decomp.),  $[\alpha]_D +62.22^{\circ}$ .

W. H. G.

**Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. VI. Action of Sulphites on Hydrazines, particularly the Naphthylhydrazines.** HANS TH. BUCHERER and MAXIMILIAN SCHMIDT (*J. pr. Chem.*, 1909, [ii], 79, 369-417. Compare Bucherer and Seyde, Abstr., 1908, i, 455).—By means of the sulphite method it is possible to pass from an amine to a phenol, thus:  $R \cdot NH_2 + 3NaHSO_3 = RO \cdot SO_2Na + Na_2SO_3 + NH_4HSO_3$ ;  $RO \cdot SO_2Na + 2NaOH = R \cdot ONa + Na_2SO_3 + H_2O$ . An analogous reaction should take place with an arylhydrazine, the only difference being the elimination of hydrazine instead of ammonia. The action of sodium hydrogen sulphite on  $\alpha$ -naphthylhydrazine and the 4-sulphonic acid has been studied, and found to follow the course indicated. The yield of hydrazine is, however, very small, owing to the occurrence of other reactions; for example, the sulphite ester formed by the action of sodium hydrogen sulphite on  $\alpha$ -naphthylhydrazine interacts with the latter substance, forming hydrazonaphthalene, thus:  $C_{10}H_7 \cdot NH \cdot NH_2 + C_{10}H_7 \cdot O \cdot SO_2Na = C_{10}H_7 \cdot NH \cdot NH \cdot C_{10}H_7 + NaHSO_3$ . The hydrazo-compound is, however, unstable, and is oxidised to the corresponding azo-compound, which combines with the hydrogen sulphite in the nascent state, forming the salt,  $C_{10}H_7 \cdot NH \cdot N(SO_3Na) \cdot C_{10}H_7$ . A small part of the hydrazonaphthalene undergoes transformation into naphthidine,

whilst another portion changes into 2:2'-dinaphtha-1:1'-carbazole with elimination of ammonia.

$\beta$ -Naphthylhydrazine does not behave exactly like the  $\alpha$ -compound. In this case the yield of hydrazine is very small, and naphthol is not produced, since the sulphite ester formed intermediately reacts at once with the naphthylhydrazine still present.

The yield of hydrazine is shown to be diminished by the destructive action of the hydrogen sulphite. It is also found that phenylhydrazine is decomposed by sodium hydrogen sulphite in a similar manner:  $2\text{NHPh}\cdot\text{NH}_2 + 4\text{NaHSO}_3 = 2\text{NHPh}\cdot\text{NH}\cdot\text{SO}_3\text{Na} + \text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$ . With the object of increasing the yield of hydrazine, therefore, an attempt was made to remove it from the destructive influence of the hydrogen sulphite by the addition of benzaldehyde. The desired result was, however, not obtained; for example, sodium  $\beta$ -naphthylhydrazine-6-sulphonate reacts with benzaldehyde, yielding the corresponding benzylidene derivative, but the latter does not react with sodium hydrogen sulphite.

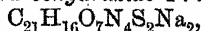
The action of sodium hydrogen sulphite on 1:1'-dinaphthylcarbamide-4:4'-disulphonic acid was also investigated. It is found that the carbamide derivative is hydrolysed with the formation of naphthionic acid, which reacts with sodium hydrogen sulphite, yielding ammonia and sodium 1-naphthylsulphite-4-sulphonate. Dinaphthylcarbohydrazidedisulphonic acid, when similarly treated, remains practically unchanged, and does not react in the manner expected, namely:  $(\text{R}\cdot\text{NH}\cdot\text{NH})_2\text{CO} + 2\text{NaHSO}_3 = 2\text{RO}\cdot\text{SO}_2\text{Na} + (\text{NH}_2\cdot\text{NH})_2\text{CO}$ .

2-Naphthylhydrazine-6-sulphonic acid,  $\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2\text{S}$ , is prepared by reducing the corresponding diazo-compound; it crystallises in microscopic prisms; the sodium salt ( $\text{H}_2\text{O}$ ) crystallises in hexagonal leaflets.

The action of sodium hydrogen sulphite on  $\beta$ -naphthylhydrazine results in the formation of sodium 1:1'-dinaphtha-2:2'-carbazole-N-sulphonate,  $\text{C}_{20}\text{H}_{12}\text{O}_3\text{NSNa}$ , crystallising in tufts of small, slender needles, 1:1'-dinaphtha-2:2'-carbazole, 2:2'-diamino-1:1'-dinaphthyl, and hydrazine.

1-Naphthylhydrazine-4-sulphonic acid, when treated with benzaldehyde and sodium hydrogen sulphite, yields sodium 1-benzylidenenaphthylhydrazine-4-sulphonate,  $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}_2\text{SNa}$ , crystallising in yellowish-white, glistening leaflets. 2-Naphthylhydrazine-6-sulphonic acid, when similarly treated, yields the corresponding benzylidene derivative, crystallising in white leaflets. Naphthionic acid, when treated with aqueous sodium hydroxide and carbonyl chloride, yields 1:1'-dinaphthylcarbamide-4:4'-disulphonic acid; the crystalline sodium salt,  $\text{C}_{21}\text{H}_{14}\text{O}_7\text{N}_2\text{S}_2\text{Na}_2$ , was analysed.

Sodium 1:1'-dinaphthylcarbohydrazide-4:4'-disulphonate,



obtained by acting on sodium 1-naphthylhydrazine-4-sulphonate with carbonyl chloride, crystallises in pink, microscopic leaflets.  $\beta$ -Azonaphthalene is not attacked when boiled with sodium hydrogen sulphite; in the presence of phenylhydrazine, however, it yields 2:2'-diamino-1:1'-dinaphthyl. Azobenzene is reduced to hydrazobenzene when treated in a similar manner.

$\beta$ -Hydroxynaphthoic acid interacts with sodium hydrogen sulphite and  $\beta$ -naphthylhydrazine, yielding sodium 1:1'-dinaphtha-2:2'-carb-

azole-N-sulphonate,  $C_{20}H_{12}O_3NSNa$ , crystallising in long needles, 2:2'-diamino-1:1'-dinaphthyl, and 1:1'-dinaphtha-2:2'-carbazole.

Similarly,  $\alpha$ -naphthylhydrazine leads to the formation of *sodium* 1:2'-dinaphtha-2:1'-carbazolesulphonate,  $C_{20}H_{12}O_3NSNa$ , crystallising in white needles,  $\alpha$ -naphthylamine, and  $\alpha$ -dinaphthylamine.

Unsuccessful attempts were made to prepare 2:2'-diamino-1:1'-dinaphthyl by the action of ammonium sulphite and ammonia on  $\beta$ -dinaphthol.

W. H. G.

**Preparation of 1-Aryl-5-halogenmethyl-2:4-dialkyl-3-pyrazolones.** FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 208593).—1-Aryl-5-methyl-2:4-dialkyl-5-pyrazolone, like the isomeric 1-aryl-3-methyl-2:4-dialkyl-5-pyrazolones, unites with bromine or chlorine, forming a dihalide, from which hydrogen halide can be eliminated with the formation of 1-aryl-5-bromomethyl-2:4-dialkyl-3-pyrazolones,  $CH_2X \cdot C \begin{smallmatrix} \nearrow NAr \cdot NR \\ \searrow CR - CO \end{smallmatrix}$ , where X is a halogen atom and R and Ar are alkyl and aryl groups respectively.

1-Phenyl-2:4-dimethyl-5-bromomethyl-3-pyrazolone, m. p. 127—130°, is thus obtained from 1-phenyl-2:4:5-trimethyl-3-pyrazolone and bromine in chloroform solution, and subsequently eliminating hydrogen bromide by the action of sodium hydroxide. By boiling this compound with water, 1-phenyl-2:4-dimethyl-5-hydroxymethyl-3-pyrazolone is produced, and by the action of diethylamine, 1-phenyl-2:4-dimethyl-5-diethylaminomethyl-3-pyrazolone (leaflets, m. p. 123°) is obtained.

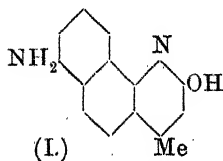
F. M. G. M.

**Quinoline Derivatives of 1:5-Naphthylenediamine.** A Case of Hydrolysis in Glacial Acetic Acid. HERMANN FINGER and C. SPIRZ (*J. pr. Chem.*, 1909, [ii], 79, 445—449).—Whilst investigating the quinoline derivatives of 1:5-naphthylenediamine, the remarkable observation was made that the diacetyl derivative of 4:10-dihydroxy-2:8-dimethyl (1:5)-naphthadiquinoline when dissolved in glacial acetic acid is hydrolysed, yielding the diacetate of the base.

1:5-Naphthylenediamine and ethyl acetoacetate interact at the ordinary temperature, yielding *ethyl* 1:5-naphthylenediaminediacetonate,  $C_{10}H_6(NH \cdot CMe \cdot CH \cdot CO_2Et)_2$ , which crystallises in glistening, silvery leaflets, m. p. 178—179°, and is converted at 220—240° into 4:10-dihydroxy-2:8-dimethyl-(1:5)-naphthadiquinoline; the diacetyl derivative of the latter substance forms small crystals, m. p. 258°.

When 1:5-naphthylenediamine and ethyl acetoacetate are heated together at 160°, they yield *bisacetoacetyl*-1:5-naphthylenediamine,  $C_{18}H_{18}O_4N_2$ , obtained as a red, crystalline substance decomposing when heated. The same reagents condense in the presence of concentrated sulphuric acid, yielding a substance which, when heated with the sulphuric acid at about 160°, is converted into 7-amino-2-hydroxy-4-methyl-1-naphthaquinoline (formula I), compact, yellow crystals, which do not melt at 300°; the diacetyl, benzoyl, and benzylidene derivatives have been prepared.

(1:5)-Naphthadiquinoline, formula II, is prepared by heating



1:5-naphthylenediamine, glycerol, sulphuric acid, and arsenious oxide together at 150°; it forms small, yellow crystals, m. p. 217—217.5°; the *dihydrochloride* and *dinitrate* were analysed. 2:8-Dimethylnaphthadiquinoline, obtained by heating 1:5-naphthylenediamine with para-aldehyde and concentrated hydrochloric acid at 100—110°, crystallises in glistening, silvery leaflets, m. p. 238—240°; the *picrate*,  $C_{18}H_{14}N_2 \cdot C_6H_3O_7N_3$ , forms yellow crystals.

1:5-Naphthylenediamine condenses with benzaldehyde and pyruvic acid in alcoholic solution, yielding 2:8-diphenyl-(1:5)-naphthadiquinoline-4:10-dicarboxylic acid, which crystallises in small, pale yellow needles. W. H. G.

[Preparation of Anthrapyridones.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 209033).—The acylaminoanthraquinones can be condensed to anthrapyridones by acid as well as alkaline condensing agents. 4-Chloro-1-anthrapyridone is obtained by heating 4-chloro-1-acetylaminanthraquinone with anhydrous sodium acetate and nitrobenzene. Anthrapyridone may be prepared by heating  $\alpha$ -acetylaminanthraquinone with anhydrous sodium acetate and acetic anhydride. F. M. G. M.

New Synthesis of *iso*Oxazoles. II. JULIUS SCHMIDT and KARL TH. WIDMANN (*Ber.*, 1909, 42, 1869—1886).—The product described as 5-methylisooxazole (Abstr., 1908, i, 457; compare Claisen, this vol., i, 185) is now shown to be a bimolecular cyanoacetone,  $(COMe \cdot CH_2 \cdot CN)_2$ ,

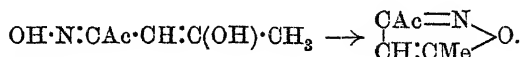
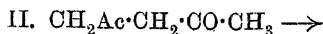
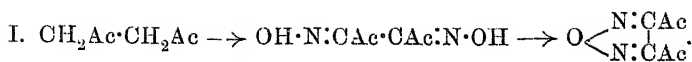
which in the course of several months sets to a hard, crystalline cake of the polymeride,  $(COMe \cdot CH_2 \cdot CN)_n$ .

The yellow oil obtained in the preparation of ethyl 5-methylisooxazole-3:4-dicarboxylate (Abstr., 1908, i, 457) is probably  $\beta$ -oximino- $\alpha\beta$ -diacetylpropionic acid,  $OH \cdot N : CAc \cdot CHAc \cdot CO_2H$ . A better yield is obtained when ethyl diacetylsuccinate is treated with fuming nitric acid at 25°. It has a penetrating odour, is distinctly acid to litmus, and decomposes when distilled under reduced pressure.

The following products have been obtained by the action of fuming nitric acid on ethyl acetylsuccinate at 15—20°: Ethyl oximinoacetylsuccinate, ethyl 5-methylisooxazole-3:4-dicarboxylate, oximino-succinic acid, (Ebert, Abstr., 1885, 1122), and ethyl  $\alpha$ -oximino-propionate (Cramer, Abstr., 1891, 823),

Ethyl  $\beta$ -oximino- $\alpha$ -acetylsuccinate,  $CO_2Et \cdot CHAc \cdot C(CO_2Et) \cdot N : OH$ , is a colourless oil, b. p. 100—105°/35 mm., and is undoubtedly an intermediate product between the acetylsuccinate and the isooxazole derivative.

The main products obtained by the action of fuming nitric acid on acetonylacetone at 10° are diacetylurazan and 4-acetyl-5-methylisooxazole, and the formation of these compounds can be represented by the following schemes:



*Diacylfurazan*,  $\begin{array}{c} \text{CAc}:\text{N} \\ \text{CAc}:\text{N} \end{array} \text{O}$ , forms colourless crystals, m. p.

127—129° (decomp.). The *dioxime*,  $\text{C}_6\text{H}_8\text{O}_2\text{N}_4$ , separates from aqueous alcohol in pale yellow crystals, which decompose at 197°. The *phenylhydrazone*,  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_4$ , forms brilliant yellow prisms, m. p. 170° (decomp.); the *p-nitrophenylhydrazone*,  $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}_5$ , brown prisms, m. p. 145—147° (decomp.), and the *semicarbazone*,  $\text{C}_4\text{H}_9\text{O}_3\text{N}_5$ , yellow plates, m. p. 185° (decomp.).

4-Acetyl-5-methylisooxazolone,  $\text{C}_6\text{H}_7\text{O}_2\text{N}$ , distils at 65—70° (20 mm.), and solidifies to a crystalline mass, which melts at about 30°. The *phenylhydrazone*,  $\text{C}_{12}\text{H}_{13}\text{ON}_3$ , forms colourless crystals, m. p. 166—168°, and the *p-nitrophenylhydrazone*,  $\text{C}_{12}\text{H}_{12}\text{O}_3\text{N}_4$ , decomposes at about 230°.

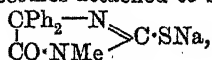
J. J. S.

**New Method for the Preparation of Thiohydantoin and the Elimination of Sulphur from them.** HEINRICH BILTZ [with P. KREBS and K. SEYDEL] (*Ber.*, 1909, 42, 1792—1800. Compare *Abstr.*, 1908, i, 462).—Benzil unites with carbamide in alcoholic alkali hydroxide solutions to form 5:5-diphenylhydantoin; apparently, in the first place diphenylglyoxalonediglycol is formed by simple addition, and this undergoes pinacolin rearrangement into the hydantoin (*Abstr.*, 1908, i, 462). This view has been confirmed by the preparation of the glycol by another method: when heated with alcoholic alkali hydroxide, it is transformed into hydantoin.

It is now shown that thiocarbamide behaves similarly, 5:5-diphenylthiohydantoin being obtained from benzil and thiocarbamide.

In the thiohydantoin, the hydrogen in position 3 is labile and replaceable by an alkali metal, which becomes, however, attached to the sulphur atom,  $\begin{array}{c} \text{CPh}_2\text{—NH} \\ \text{CO—N} \end{array} \gg \text{C}\cdot\text{SNa}$ , and is easily replaced by methyl.

Thiohydantoin already substituted in position 3, likewise dissolve in alkali hydroxides; here the imide hydrogen (position 1) is replaced by metal, which again becomes attached to sulphur,



and is again easily replaced by methyl. Two isomeric monomethyl and two dimethyl derivatives of diphenylthiohydantoin are thus obtained.

Sulphur is easily removed from the thiohydantoin by the action of bromine water in alcoholic solution, or by boiling with dilute sulphuric acid, or by oxidation with permanganate in alkaline solution, the two last methods having the advantage that further substitution cannot occur. In the case of 5:5-diphenyl-1:3-dimethylthio-

hydantion, these methods fail, but sulphur is easily eliminated by heating in acetic acid solution with mercuric oxide.

5:5-Diphenylthiohydantoin forms short prisms, m. p. 235°. Small quantities of diphenylacetylenedithiodiurein (Anschütz and Geldermann, Abstr., 1891, 725) are formed at the same time. 5:5-Diphenyl-2-methylthiohydantoin crystallises in well-formed prisms, m. p. 207°. 5:5-Diphenyl-3-methylthiohydantoin forms colourless needles, m. p. 185°. 5:5-Diphenyl-2:3-dimethylthiohydantoin crystallises in monoclinic prisms, m. p. 168°. 4:5-Dihydroxy-2-thiol-4:5-diphenyl-1:3-dimethyl-tetrahydroglyoxaline, prepared by condensing benzil with dimethylthiocarbamide, forms crystals, m. p. 158—159°. When melted it loses a molecule of water and forms 5:5-diphenyl-1:3-dimethylthiohydantoin, which crystallises in lustrous, colourless plates, m. p. 141—142°.

5:5-bis-p-Methoxyphenylthiohydantoin, prepared from anisil and thiocarbamide, separates in colourless plates, m. p. 188°. E. F. A.

**Electric Conductivity of Certain Dye-baths.** LEO VIGNON (*Bull. Soc. chim.*, 1909, [iv], 5, 495—500. Compare this vol., i, 298).—Measurements have been made of the concentrations at which dye-baths containing orange II, roccellin, or magenta, dye wool, and of the electric conductivities of such baths. The results show that baths containing any one of these dyes are strongly ionised, and that these substances do not dye until the conductivity of the solution has attained a certain value. In practice this increase of conductivity can be secured by heating the bath, adding more dye, or by the addition of sulphuric acid, etc. Effective dyeing depends, not only on the intensity of the ionisation, but also on the nature of the ions present; thus magenta dyes wool in neutral or faintly acid solutions, but not in presence of sodium hydroxide. T. A. H.

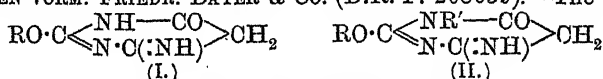
**Combination of Silica with Methylene-blue.** LOUIS PELET-JOLIVET and N. ANDERSEN (*Bull. Soc. chim.*, 1909, [iv], 5, 540—546).—In a previous investigation Pelet-Jolivet and Grand showed that amorphous silica, when placed in a solution of methylene-blue, absorbs the colouring matter, the amount absorbed depending on the concentration of the solution (*Rev. Mat. Col.*, 1907, August). In the present paper the composition of the precipitates formed when solutions of methylene-blue are added to solutions of water-glass are dealt with. These precipitates are not definite compounds, but merely mixtures of colouring matter, silica, and water, the relative proportion of each depending on the concentration of the solutions employed, according to the law of adsorption. Thus, when solutions of methylene-blue of different concentrations are added to a solution of water-glass of the same strength, the amount of methylene-blue in the precipitate formed increases with the strength of methylene-blue solution added. It is probable that, as shown by Kalensky in his experiments on the precipitation of water-glass solutions by ferric chloride, the active ions present have some influence on the composition of the precipitate formed, negative ions augmenting the quantity of positive colloid, and positive ions that of the negative

colloid. The fresh precipitates when washed yield colouring matter to water, slightly at first, and then in increasing quantities as the sodium chloride is washed out of the precipitate, but they yield dye to water much less readily after being dried at atmospheric temperature for some days.

Methylene-blue adsorbed by calcined precipitated silica is not entirely removed by water or by subsequent extraction with alcohol, although the latter never comes away quite colourless. The colouring matter dissolved by these solvents from such preparations differs in no respect from the original dye. These results are not in accordance with those obtained by Suida (*Zeit. Farb. Ind.*, 1907, November), who found that the precipitates yielded by magenta with solutions of water-glass were of constant composition. T. A. H.

**Polyiodo-derivatives.** LOUIS PELET-JOLIVET and H. SIEGRIST (*Bull. Soc. chim.*, 1909, [iv], 5, 626—628).—When to portions of a solution of methylene-blue or safranin varying quantities of a solution of iodine in potassium iodide are added, the amount of iodine which combines with the dye increases with the concentration of the initial mixture in iodine, but not quite regularly. If  $C$  represents the final concentration of free iodine, and  $x$  the iodine fixed by the dye, these have the relation  $x = \beta C^{1/p}$ , where  $\beta = 2.6$  for methylene-blue and  $1.75$  for safranin, and  $1/p = 0.085$  for methylene-blue and  $0.12$  for safranin. These periodides are therefore adsorption compounds. In estimating the iodine in the periodides, volumetric determination with sodium thio-sulphate was resorted to. This gives only the value  $I_x$  in the periodides, which may be represented by the general formula  $BI_{I_x}$ . T. A. H.

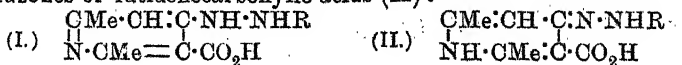
**Preparation of 2-Alkyloxy-1-alkylpyrimidines.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 208639).—The 2-alkyl-



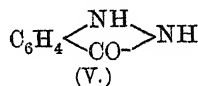
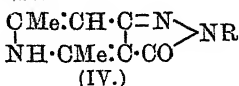
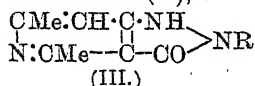
oxypyrimidines (I) are readily alkylated in position 1, and give rise to 2-alkyloxy-1-alkylpyrimidines (II), which are intermediate products in the hitherto unaccomplished synthesis of the 1-alkyl-xanthines.

4-Imino-2-methoxy-1-methyl-6-pyrimidone, m. p.  $216^\circ$ , results from the action of methyl sulphate and aqueous sodium hydroxide on 4-imino-2-methoxy-6-pyrimidone. F. M. G. M.

**Some Derivatives of Ethyl 4-Chlorolutidine-3-carboxylate [Ethyl 4-Chloro-2:6-dimethylnicotinate].** AUGUST MICHAELIS (*Annalen*, 1909, 366, 324—407).—An extension of the investigations commenced by Michaelis and von Arend (*Abstr.*, 1901, i, 609; 1903, i, 292) and Michaelis and Hanisch (*Abstr.*, 1902, i, 823). The condensation of hydrazines with ethyl 4-chloro-2:6-dimethylnicotinate leads first to the formation of esters of acids, which may be regarded as arylhydrazinolutidinecarboxylic acids (I), or arylhydrazones of lutidonecarboxylic acids (II):

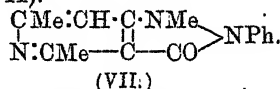
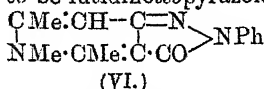


The latter assumption is the more probable, however, since the anhydrides of these compounds are yellow, a fact better represented by (IV) than (III), since benzoisopyrazolone, which undoubtedly has the constitution (V), is colourless.

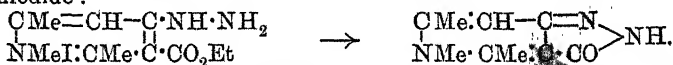


However, although the acids are probably lutidonehydrazonocarboxylic acids, nevertheless they react sometimes as hydrazinolutidinecarboxylic acids; thus, with phosphoryl chloride they yield 3-chloroindazoles, and when treated with mercuric oxide are converted into the corresponding azo-derivatives.

The lutidonehydrazonocarboxylic acids combine with alkyl iodides, forming compounds which, when acted on by alkali, lose hydrogen iodide with the formation of white, crystalline substances, which were formerly regarded as alkyl-lutidonopyrazolones (VI), but which are now shown to be lutidinoisopyrazolones (VII).



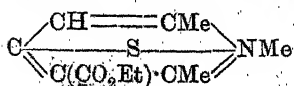
The alkyl-lutidonopyrazolones, in agreement with the constitution represented by (VI), are yellow substances. They are prepared by the action of sodium hydroxide on the hydrazino-ester formed by the condensation of hydrazines with ethyl 4-chloro-2:6-dimethylnicotinate methiodide:



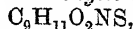
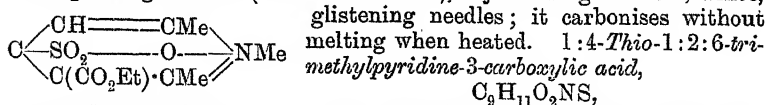
I. *Preparation and Properties of Ethyl 4-Chloro-2:6-dimethylnicotinate*.—The formation of this ester by the action of phosphoryl chloride on ethyl aminocrotonate takes place through the intermediate formation of *ethyl 2:6-dimethyl-4-pyridone-3-carboxylate*,  $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}$ , since this substance is always obtained as a by-product, and is converted by phosphoryl chloride into ethyl 4-chloro-2:6-dimethylnicotinate; it crystallises in white prisms, m. p.  $161^\circ$ ; the corresponding acid has m. p.  $251^\circ$  (compare Collie, Trans., 1891, 59, 176).

*Ethyl 4-chloro-2:6-dimethylnicotinate methiodide*,  $\text{C}_{11}\text{H}_{15}\text{O}_3\text{NCl}$ , prepared by the action of potassium iodide on the product of the interaction of ethyl chlorodimethylnicotinate and methyl sulphate, crystallises in white needles, m. p.  $137^\circ$ . *Ethyl 4-iodo-2:6-dimethylnicotinate methiodide*,  $\text{C}_{11}\text{H}_{15}\text{O}_3\text{NI}$ , prepared by heating the 4-chloro-ester with an excess of methyl iodide, forms pale yellow, hexagonal prisms, m. p.  $194^\circ$ .

[With WILHELM HEYDEN.]—II. *Thio-derivatives of Ethyl 4-Chloro-2:6-dimethylnicotinate*.—*Ethyl 1:4-thio-1:2:6-trimethylpyridine-3-carboxylate* (annexed formula), prepared by the action of potassium hydrogen sulphide on the condensation product of ethyl chlorodimethylnicotinate and methyl sulphate, crystallises in yellow, glistening plates or long, flat needles, m. p.  $175^\circ$ ; the hydrochloride,  $\text{C}_{11}\text{H}_{15}\text{O}_2\text{NS} \cdot \text{HCl}$ , forms glistening, white plates, m. p.



170°; the *platinichloride*,  $(C_{11}H_{15}O_2NS)_2 \cdot H_2PtCl_6$ , is a yellow powder, m. p. 215°; the *hydriodide* forms white needles, m. p. 140°; the *methiodide*,  $C_{12}H_{18}O_2NSI$ , crystallises in colourless, glistening needles, m. p. 185°. The thio-ester is oxidised by chlorine, hydrogen peroxide, etc., to the corresponding *trioxide* (annexed formula), crystallising in short, white,

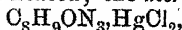


prepared by hydrolysing the ester with alcoholic potassium hydroxide, forms small, yellow, glistening crystals, m. p. 241°; the *ammonium* salt crystallises in slender, glistening needles; the *methiodide* forms white prisms, m. p. 230°; the *trioxide*,  $C_9H_{11}O_6NS$ , forms small, white crystals, decomposes above 200°, and yields a *mercury* salt,  $(C_9H_{10}O_6NS)_2Hg$ , a white, microcrystalline powder.

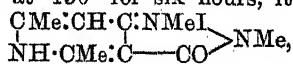
III. *Anilino-derivatives of Ethyl 4-Chloro-2:6-dimethylnicotinate*.—Aniline reacts energetically with the methiodide or methosulphate of ethyl chlorodimethylnicotinate, yielding ethyl 4-anilino-2:6-dimethylnicotinate, and also a crystalline substance, m. p. 233°, which is probably a mixture of the *methoxydioxide* of ethyl 4-anilino-2:6-dimethylnicotinate and *ethyl 4-methylanilino-2:6-dimethylnicotinate*. Aniline and ethyl chlorodimethylnicotinate when heated together yield 4-anilino-2:6-dimethylnicotinic acid and its ethyl ester. *Ethyl 4-anilino-2:6-dimethylnicotinate*,  $C_{16}H_{18}O_2N_2$ , crystallises with  $1H_2O$  in long, white needles, m. p. 80°; the *anhydrous* substance has b. p. 164°/15 mm.; the *hydrochloride*,  $C_{16}H_{18}O_2N_2 \cdot HCl$ , crystallises in prisms, m. p. 168–169°; the *platinichloride* crystallises in thin, red leaflets, m. p. 194° (decomp.); the *hydriodide* crystallises in needles, m. p. 187°, and when heated in a vacuum dissociates into anilinolutidine, ethyl iodide, and carbon dioxide.

4-Anilino-2:6-dimethylnicotinic acid,  $C_{14}H_{14}O_2N_2$ , crystallises with  $1H_2O$  in glistening, white needles, m. p. 244°; the *silver* salt is a white, amorphous powder; the *methiodide*,  $C_{15}H_{17}O_2N_2I$ , forms white leaflets, m. p. 200°; the *platinichloride*,  $(C_{15}H_{16}O_2N_2)_2 \cdot H_2PtCl_6$ , of the corresponding methochloride forms reddish-yellow needles, m. p. 230°.

IV. *Hydrazine Derivatives of Ethyl 4-Chloro-2:6-dimethylnicotinate*. [With LUDWIG KRIETEMEYER].—Lutidonopyrazolone, described previously (*loc. cit.*) as hydrazinodimethylnicotinic anhydride, forms a *hydrochloride*,  $C_8H_9ON_3 \cdot HCl$ , white, glistening crystals, which decompose without melting when heated; the *mercurichloride*,



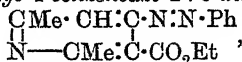
forms tufts of long, colourless needles, m. p. 240°. When lutidonopyrazolone is heated with methyl iodide at 150° for six hours, it yields *lutidonomethylpyrazolone methiodide*,



crystallising in slender, yellow needles, m. p. 254–255°.

Lutidonephenylhydrazoncarboxylic acid (2:6-dimethyl-4-pyridone-phenylhydrazon-3-carboxylic acid) has been described previously (Michaelis and von Arend, *loc. cit.*); the *platinichloride* forms bright yellow needles, and decomposes without melting when heated. The

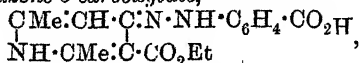
ethyl ester,  $\text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{N} \cdot \text{NHPH}$   
 $\text{NH} \cdot \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et}$ , crystallises in white or faintly yellow  
 prisms, m. p.  $141^\circ$ , and when warmed in alcoholic solution with yellow  
 mercuric oxide yields ethyl 4-benzeneazo-2:6-dimethylnicotinate,



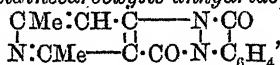
crystallising in dark red needles, m. p.  $78^\circ$ . The following derivatives  
 of 2:6-dimethyl-4-pyridonephenylhydrazone-3-carboxylic acid were  
 prepared by heating this substance with the corresponding halogen  
 compound: methiodide,  $\text{C}_5\text{H}_2\text{NMe}_2 \cdot \text{CO}_2\text{H}$   
 $\text{NMeI} \cdot \text{NHPH}$ , pale yellow leaflets,

m. p.  $288^\circ$ ; ethiodide,  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_3\text{EtI}$ , tufts of pale yellow needles,  
 m. p.  $218^\circ$ ; propiodide,  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_3\text{PrI}$ , yellow needles, m. p.  $207^\circ$ ;  
 benzylochloride,  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_3 \cdot \text{CH}_2\text{PhCl}$ , white leaflets, m. p.  $252^\circ$ ;  
 phenacylbromide,  $\text{C}_{14}\text{H}_{15}\text{O}_2\text{N}_3 \cdot \text{Ph} \cdot \text{CO} \cdot \text{CH}_2\text{Br}$ , white, transparent prisms,  
 m. p.  $288^\circ$ .

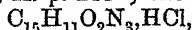
[With DIETRICH REINIGHAUS.]—Ethyl 2:6-dimethyl-4-pyridone-o-  
 carboxyphenylhydrazone-3-carboxylate,



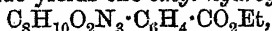
prepared by the condensation of ethyl chlorodimethylnicotinate and  
 o-hydrazinobenzoic acid, crystallises in small, orange needles, sinters at  
 $180^\circ$ , and melts with the elimination of water and alcohol at  $285^\circ$ , the  
 m. p. of the anhydride; the ammonium salt is a reddish-yellow, crystal-  
 line powder, m. p.  $189-190^\circ$ . The formation of the ester just  
 described is accompanied by that of lutidinobenzobisisopyrazolone (o-carb-  
 oxyphenylhydrazinolutidinecarboxylic anhydride),



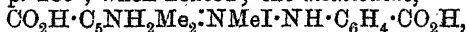
a pink, crystalline powder, m. p.  $285^\circ$ ; the hydrochloride,



forms brown, glistening leaflets, m. p.  $285^\circ$  (decomp.). The pyrazolone  
 is hydrolysed by 10% aqueous sodium hydroxide, yielding 2:6-dimethyl-  
 4-pyridone-o-carboxyphenylhydrazone-3-carboxylic acid,  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3$ ,  
 which crystallises in glistening, yellow needles, loses water when  
 heated, and melts at  $285^\circ$ , the m. p. of the anhydride; the hydro-  
 chloride,  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3 \cdot \text{HCl}$ , forms small, greyish-white crystals; the  
 platinichloride forms golden-yellow, glistening leaflets; the sodium  
 hydrogen salt,  $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_3\text{Na} \cdot 2\text{H}_2\text{O}$ , crystallises in pale yellow needles;  
 the barium hydrogen salt,  $(\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_3)_2\text{Ba}$ , forms yellow needles; the  
 hydrogen silver salt,  $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_3\text{Ag}$ , is a pale yellow powder, and when  
 treated with ethyl iodide yields the ethyl hydrogen ester,



which crystallises in small, yellow needles and passes into the  
 anhydride, m. p.  $285^\circ$ , when heated; the methiodide,

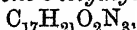


crystallises in white needles, m. p.  $211^\circ$ . The following compounds  
 are prepared by methods similar to those employed in the formation of  
 the analogous ortho-compounds: ethyl 2:6-dimethyl-4-pyridone-m-carb-  
 oxyphenylhydrazone-3-carboxylate, yellow, crystalline powder, m. p.

300° (decomp.); the *platinichloride* forms small, golden-yellow crystals, m. p. 218° (decomp.); the *acid*,  $C_{15}H_{14}O_4N_2 \cdot 2H_2O$ , forms slender, white needles, m. p. 234°.

[With BENNO VON GHIEL.]—2:6-Dimethyl-4-pyridone-*p*-tolylhydrazone-3-carboxylic acid,  $C_{14}H_{16}N_2 \cdot CO_2H$ , prepared from ethyl chlorodimethylnicotinate and *p*-tolylhydrazine, forms a yellow, microcrystalline powder, m. p. 283°; it does not yield an anhydride when heated; the *ethyl ester*,  $C_{14}H_{16}N_2 \cdot COEt$ , forms faintly yellow, felted needles, m. p. 154°; the *hydrochloride*,  $C_{15}H_{17}O_2N_2 \cdot HCl \cdot H_2O$ , forms yellowish-white needles, m. p. 270°; the *platinichloride* crystallises in brown needles, and decomposes without melting when heated; the *mercurichloride*,  $C_{15}H_{17}O_2N_2 \cdot HgCl_2$ , forms white needles, m. p. 131°; the *methiodide*,  $C_{15}H_{17}O_2N_2 \cdot MeI$ , forms pale yellow leaflets, m. p. 236°.

*Ethyl 2:6-dimethyl-4-pyridone-o-tolylhydrazone-3-carboxylate*,



crystallises in white leaflets, m. p. 108°; the solution obtained by boiling the ester with aqueous sodium hydroxide when treated with carbon dioxide does not yield the corresponding acid, but the *anhydride*

(*lutidino-o-tolylpyrazolone*),  $\begin{array}{c} CMe:CH-C=N \\ NH \cdot CMe:C \cdot CO \end{array} > N \cdot C_6H_4Me$ , yellow needles,

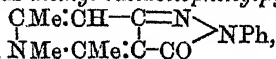
which decompose without melting above 310°; the *mercurichloride*,  $C_{15}H_{15}ON_3 \cdot HgCl_2$ , forms white or slightly pink needles, m. p. 223°; the *methiodide*,  $C_{15}H_{15}ON_3 \cdot MeI$ , crystallises in pale yellow leaflets, m. p. 268°.

[With LUDWIG KRIETEMEYER.]—2:6-Dimethyl-4-pyridone- $\beta$ -naphthylhydrazone-3-carboxylic acid,  $C_{18}H_{17}O_2N_3$ , crystallises in yellow needles, m. p. 288°; the *hydrochloride* was analysed.

*Ethyl 4-hydrazino-2:6-dimethylnicotinate methiodide*, prepared by the action of hydrazine on ethyl 4-chloro-2:6-dimethylnicotinate methiodide, forms yellow needles, m. p. 247°, and is converted by aqueous sodium hydroxide into *methyl-lutidonopyrazolone*,  $\begin{array}{c} CMe:CH-C=N \\ NMe \cdot CMe:C \cdot CO \end{array} > NH$ ,

which crystallises with  $4H_2O$  in slender, yellow needles, m. p. above 360°; the *hydrochloride* of the latter compound ( $1H_2O$ ) forms white crystals, melting above 360° with elimination of methyl chloride; the *platinichloride*,  $(C_9H_{11}ON_3)_2 \cdot H_2PtCl_6$ , forms brownish-red needles, m. p. above 360°; the *hydriodide* ( $1\frac{1}{2}H_2O$ ) forms white needles, and loses methyl iodide without melting when heated above 360°.

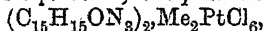
*Ethyl 4-phenylhydrazino-2:6-dimethylnicotinate methiodide* forms thick, yellowish-red prisms, m. p. 203°, and when treated with aqueous sodium hydroxide yields *methyl-lutidonophenylpyrazolone*,



which forms yellow crystals, m. p. 258°; the *hydrochloride* ( $3H_2O$ ) of the latter substance crystallises in white needles, m. p. 255°; the *platinichloride*,  $(C_{15}H_{15}ON_3)_2 \cdot H_2PtCl_6$ , is a yellowish-red powder, m. p. above 360°; the *hydriodide* ( $2H_2O$ ) forms colourless needles, m. p. 230°; the *methiodide* ( $1H_2O$ ) has m. p. 145°; the *anhydrous substance* has m. p. 220°.

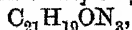
*Lutidinodimethylisopyrazolone*,  $\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NMe} \\ \text{N} : \text{CMe} - \text{C} - \text{CO} \end{array} \text{NMe}$ , prepared by the action of aqueous sodium hydroxide or silver oxide on the product of the interaction of methyl iodide and lutidonopyrazolone, crystallises with  $2\text{H}_2\text{O}$  in white, glistening prisms, m. p.  $92^\circ$ ; the *anhydrous* substance has m. p.  $167^\circ$ ; the *hydrochloride*,  $\text{C}_{10}\text{H}_{13}\text{ON}_3 \cdot \text{HCl}$ , is a crystalline mass, m. p. above  $360^\circ$ ; the *platinichloride* forms stout, yellow needles, m. p.  $230^\circ$ ; the *methiodide*,  $\text{C}_{10}\text{H}_{13}\text{ON}_3 \cdot \text{MeI}$ , forms pale yellow needles, m. p.  $276^\circ$ , and when treated with a concentrated aqueous solution of sodium hydroxide yields *lutidinodimethylpyrazolone-methylammonium hydroxide*; the latter substance, when treated with hydrochloric acid and platinic chloride, yields the *methochloride platinichloride*, reddish-yellow crystals, m. p.  $255^\circ$  (decomp.).

[With THILO MÜHLBERG.]—*Lutidinophenylmethylisopyrazolone* (*lutidinoantipyrine*),  $\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NMe} \\ \text{N} : \text{CMe} - \text{C} - \text{CO} \end{array} \text{NPh}$ , prepared by the action of sodium hydroxide on 2:6-dimethyl-4-pyridonephenylhydrazone-3-carboxylic acid methiodide, crystallises in white leaflets or needles, m. p.  $154^\circ$ ; it also crystallises with  $12\text{H}_2\text{O}$  in broad needles; the *hydrochloride*,  $\text{C}_{15}\text{H}_{15}\text{ON}_3 \cdot \text{HCl}$ , forms white, glistening leaflets, m. p.  $286\text{--}287^\circ$  (decomp.); the *platinichloride* ( $1\text{H}_2\text{O}$ ) forms slender, golden-yellow needles, which decompose without melting when heated; the methiodide is identical with the methiodide of methyl-lutidonophenylpyrazolone; the *methochloride*,  $\text{C}_{15}\text{H}_{15}\text{ON}_3 \cdot \text{MeCl} \cdot \text{H}_2\text{O}$ , forms slender, white needles, m. p.  $174^\circ$ ; the *platinichloride*,

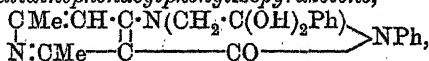


forms small, golden-yellow crystals, and decomposes without melting at high temperatures; the *ethiodide*,  $\text{C}_{15}\text{H}_{15}\text{ON}_3 \cdot \text{EtI} \cdot \text{H}_2\text{O}$ , forms leaflets, m. p.  $200^\circ$ ; the *propiodide*,  $\text{C}_{15}\text{H}_{15}\text{ON}_3 \cdot \text{PrI}$ , crystallises in leaflets, m. p.  $270^\circ$ . The parent substance when treated with bromine in glacial acetic acid yields the *dibromide*,  $\begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NMe} \\ \text{NBr}_2 : \text{CMe} - \text{C} - \text{CO} \end{array} \text{NPh}$ , crystallising in yellowish-red needles, m. p.  $180^\circ$  (decomp.). A *tetraiodide*, crystallising in red needles, m. p.  $182^\circ$ , was also prepared.

The following compounds are prepared by methods similar to those already described. *Lutidinophenylethylisopyrazolone*,  $\text{C}_{16}\text{H}_{17}\text{ON}_3$ , forms slender, white needles, m. p.  $132^\circ$ ; the *dibromide*,  $\text{C}_{16}\text{H}_{17}\text{ON}_3 \cdot \text{Br}_2$ , forms dark orange crystals, m. p.  $180^\circ$ . *Lutidinophenylpropylisopyrazolone*,  $\text{C}_{17}\text{H}_{19}\text{ON}_3$ , crystallises in small, slender needles, m. p.  $128^\circ$ ; the *methiodide* has m. p.  $228^\circ$ . *Lutidinophenylbenzylisopyrazolone*,



forms white needles, m. p.  $133^\circ$ ; the *methiodide* forms yellow needles, m. p.  $230^\circ$ . *Lutidinophenacylphenylisopyrazolone*,

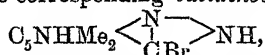


crystallises with  $2\text{H}_2\text{O}$  in colourless, transparent prisms, m. p.  $143^\circ$ ; it crystallises from alcohol in anhydrous, colourless leaflets, m. p.  $180^\circ$ . The molecule of water combined with the phenacyl radicle cannot be removed without destroying the substance. *Lutidinopolylmethylisopyrazolone*,  $\text{C}_{16}\text{H}_{17}\text{ON}_3$ , forms snow-white leaflets, m. p.

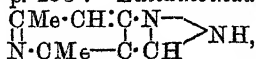
145°; the corresponding *o*-tolyl derivative forms white needles, m. p. 132°.

V. *Indazoles and Chloroindazoles of Lutidines*.—The lutidone-hydrazonecarboxylic acids, when heated with phosphoryl chloride or bromide, yield the corresponding chloro- or bromo-indazoles, which, when treated with zinc dust and acetic acid, yield the indazoles.

*Lutidino-3-chloroindazole hydrochloride*,  $C_8H_8N_3Cl \cdot HCl$ , forms colourless needles, m. p. 310°; the *platinichloride* ( $2H_2O$ ) is a reddish-yellow crystalline powder; the corresponding *lutidinobromoindazole*,



forms white needles, m. p. 253°. *Lutidinoindazole*,

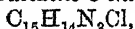


prepared by reducing the bromo-, but not the chloro-, derivative, forms aggregates of needles, m. p. 190°.

[With LUDWIG KRIETEMEYER.]—The following lutidino-3-chloro-2-alkylindazoles are prepared by heating lutidino-3-chloroindazole with alcoholic potassium hydroxide and alkyl iodide. *Lutidino-3-*

*chloro-2-methylindazole*,  $C_8NHMe_2 \begin{array}{c} \diagup N \diagdown \\ | \\ CCl \end{array} CMe$ , forms white needles,

m. p. 74°; the *platinichloride* crystallises in bright yellow needles, m. p. 240° (decomp.). *Lutidino-3-chloro-2-ethylindazole*,  $C_{10}H_{12}N_3Cl$ , has m. p. 118°; the *platinichloride* ( $1H_2O$ ) forms red crystals, which swell at 219°, m. p. 224°. *Lutidino-3-chloro-2-benzylindazole*,



crystallises in white needles, m. p. 95°.

[With DIETRICH REINIGHAUS.]—*Lutidino-3-chloro-2-m-carboxyphenylindazole*,  $C_8NHMe_2 \begin{array}{c} \diagup N \diagdown \\ | \\ CCl \end{array} N \cdot C_6H_4 \cdot CO_2H$ , is a white, crystalline

powder, m. p. 195° (decomp.); the *sodium salt* ( $1H_2O$ ) was prepared; the *methiodide* crystallises in small, white needles, m. p. 239° (decomp.); the *ethyl ester*,  $C_{14}H_{11}N_3Cl \cdot CO_2Et$ , forms yellowish-white crystals, m. p. 124°. *Lutidino-2-m-carboxyphenylindazole*,  $C_{15}H_{13}O_2N_3$ , crystallises with  $2H_2O$  in white, microscopic crystals, m. p. 165°.

[With BENNO VON GHIEL.]—*Lutidino-3-chloro-2-p-tolylindazole*,

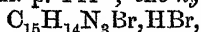


forms white, rhombohedral crystals, m. p. 174°; the *methiodide* crystallises in slender, pale yellow needles, m. p. 246–247°; the *methochloride* has m. p. 231–232°. The corresponding 3-bromo-compound,  $C_{15}H_{14}N_3Br$ , forms white needles, m. p. 161°.

*Lutidino-2-p-tolylindazole*,  $C_{15}H_{15}N_3$ , crystallises in white, felted needles, m. p. 131–132°; the *hydrochloride* forms slender, white needles, m. p. 293°; the *methiodide* crystallises in long needles, m. p. 252°. *Lutidinobromo-2-p-tolylindazole*,



crystallises with  $2\text{H}_2\text{O}$  in long, white needles, m. p.  $133^\circ$ ; the *anhydrous* substance has m. p.  $141^\circ$ ; the *hydrobromide*,



is obtained by the action of hydrogen bromide in glacial acetic acid on lutidino-2-*p*-tolylindazole; it forms white needles and does not melt below  $290^\circ$ .

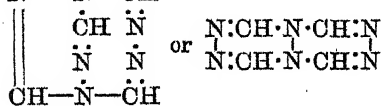
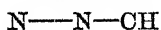
*Lutidino-3-chloro-2-o-tolylindazole* forms rhombic prisms, m. p.  $157^\circ$ ; the *methiodide* crystallises in pale yellow needles, m. p.  $138^\circ$ ; the 3-*bromo*-derivative,  $\text{C}_{15}\text{H}_{14}\text{N}_8\text{Br}$ , has m. p.  $155^\circ$ . *Lutidino-2-o-tolylindazole* forms white needles, m. p.  $121^\circ$ ; the *hydriodide* crystallises in bright yellow needles, m. p.  $205^\circ$ .

[With LUDWIG KRIETEMEYER.]—*Lutidino-3-chloro-2-β-naphthylindazole*,  $\text{C}_{18}\text{H}_{14}\text{N}_8\text{Cl}$ , crystallises in yellowish-white needles, m. p.  $190^\circ$ ; the *methiodide* has m. p.  $301^\circ$  (decomp.); the *methochloride* has m. p.  $264^\circ$ . *Lutidino-3-bromo-2-β-naphthylindazole* forms small, white needles, m. p.  $180^\circ$ . *Lutidino-2-β-naphthylindazole*,  $\text{C}_{18}\text{H}_{15}\text{N}_8$ , crystallises in white prisms, m. p.  $175^\circ$ ; the *methiodide* forms white needles, m. p.  $264^\circ$  (decomp.).

W. H. G.

**1-Amino-1:3:4-triazole.** GUIDO PELLIZZARI (*Gazzetta*, 1909, 39, i, 520—540. Compare Abstr., 1901, i, 570, 571).—Diformylhydrazine may be prepared more readily (77% yield) by the action of dry sodium formate on hydrazine sulphate than by the interaction of ethyl formate on hydrazine hydrate (compare Curtius, Schöfer, and Schwan, Abstr., 1895, 263).

When heated at  $160^\circ$ , diformylhydrazine yields 1-amino-1:3:4-triazole and diazodimethinetetrazoline (*vide infra*). 1-Amino-1:3:4-triazole *platinichloride*,  $(\text{C}_2\text{H}_4\text{N}_4)_2\cdot\text{H}_2\text{PtCl}_6$ , has m. p.  $230^\circ$  (decomp.). The *tetrachloroplatato*-compound,  $(\text{C}_2\text{H}_4\text{N}_4)_2\cdot\text{PtCl}_4$ , and the *trichloroaurico*-compound,  $\text{C}_2\text{H}_4\text{N}_4\cdot\text{AuCl}_3$ , explode on heating; the *aurichloride*,  $\text{C}_2\text{H}_4\text{N}_4\cdot\text{HAuCl}_4\cdot\text{H}_2\text{O}$ , has m. p.  $120^\circ$  or  $170^\circ$  (anhydrous).



acid, decomposes into hydrazine, formic acid, and 1:3:4-triazole.

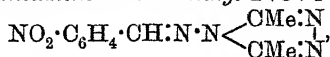
*Diazodimethinetetrazoline* (annexed formula) crystallises from alcohol in small, elongated plates, m. p.  $263^\circ$  (decomp.), has the normal molecular weight in boiling water, and, when boiled with hydrochloric

1-Amino-2:5-dimethyl-1:3:4-triazole,  $\text{NH}_2\cdot\text{N} \begin{array}{l} \text{CMe:N} \\ \text{CMe:N} \end{array}$ , prepared

either by heating acetylhydrazine at  $180^\circ$  or by heating diacetylhydrazine at  $180$ — $190^\circ$  and boiling the acetylaminodimethyltriazole thus obtained with sulphuric acid, crystallises from alcohol in large, colourless prisms, m. p.  $196^\circ$ . The hydrochloride, m. p.  $228^\circ$  (Silberrad, Trans., 1900, 1185, gave m. p.  $232^\circ$ ); *sulphate*,  $(\text{C}_4\text{H}_8\text{N}_4)_2\cdot\text{H}_2\text{SO}_4$ , m. p.  $230^\circ$ ; *platinichloride*,  $(\text{C}_4\text{H}_8\text{N}_4)_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$ , m. p.  $260^\circ$  (anhydrous) (compare Ruhemann and Merriman, Trans., 1905, 87, 1768), and the *tetrachloroplatato*-derivative,  $(\text{C}_4\text{H}_8\text{N}_4)_2\cdot\text{PtCl}_4$ , were prepared.

1-Acetylamino-2:5-dimethyl-1:3:4-triazole,  $\text{NHAc} \cdot \text{N} \begin{smallmatrix} \text{CMe} \cdot \text{N} \\ \text{CMe} \cdot \text{N} \end{smallmatrix}$ ,  
separates from acetone in prismatic crystals, m. p. 163°.

1-m-Nitrobenzylideneamino-2:5-dimethyl-1:3:4-triazole,



prepared by the action of *m*-nitrobenzaldehyde on 1-amino-2:5-dimethyl-1:3:4-triazole in presence of piperidine, separates from benzene in shining crystals, m. p. 183°.

T. H. P.

**Quinonoid Compounds. XIII. Aniline-Black. II.** RICHARD WILLSTÄTTER and STEFAN DOROGI (*Ber.*, 1909, 42, 2147—2168. Compare Abstr., 1907, i, 641).—The authors have undertaken the study of the constitution and mode of formation of aniline-black with the object of explaining its formation as an intermediate product in the oxidation of aniline to benzoquinone. It is found that 1 molecule of aniline requires 1·27 atoms of oxygen for its oxidation to aniline-black by means of potassium dichromate and sulphuric acid at 5°; a very pure form of aniline-black can be obtained by using only sufficient dichromate to oxidise about a quarter of the total aniline present; by this means over oxidation of the aniline-black is prevented; the precipitated aniline-black sulphate when filtered off and washed with water forms a chrome-green powder; it was further purified by shaking for twelve to twenty-four hours with 100 times its weight of 2*N*-sulphuric acid and then boiling for six hours more with fresh acid, and was finally converted into the colour base by adding it to a large excess of boiling 2*N*-ammonia solution. Aniline-black,  $\text{C}_{48}\text{H}_{36}\text{N}_8$ , thus prepared is a dark blue powder, the composition of which may be expressed by the formula:

$\text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$ .  
When heated with 17% sulphuric acid for twelve hours in a sealed tube at 200°, it loses one-eighth part of its nitrogen in the form of ammonia, according to the equation:  $\text{C}_{48}\text{H}_{36}\text{N}_8 + \text{H}_2\text{O} = \text{C}_{48}\text{H}_{35}\text{ON}_7 + \text{NH}_3$ . The resulting product is a much darker aniline-black; a description of this substance and of its salts is reserved for a future communication.

The aniline-black of the composition  $\text{C}_{48}\text{H}_{36}\text{N}_8$  yields green salts, the *hydrochloride* and *sulphate* having the formulæ  $\text{C}_{48}\text{H}_{36}\text{N}_8 \cdot 3\text{HCl}$  and  $\text{C}_{48}\text{H}_{36}\text{N}_8 \cdot 2\text{H}_2\text{SO}_4$  respectively; a second sulphate of the formula  $\text{C}_{48}\text{H}_{36}\text{N}_8 \cdot 5\text{H}_2\text{SO}_4$  is obtained by shaking the former sulphate with an ethereal solution of sulphuric acid; it is an almost black solid. The authors have also made quantitative measurements of the amount of benzoquinone produced by the oxidation of *p*-aminophenol, *p*-phenylenediamine, aniline, aniline-black, benzoquinonemonoanil, and phenylhydroxylamine with dichromate and sulphuric acid and with lead peroxide and sulphuric acid.

P. H.

[Cain's Theory of Diazonium and Ammonium Salts.]  
ARTHUR HANTZSCH (*Ber.*, 1909, 42, 2137—2138).—Polemical. A final reply to Cain (this vol., i, 445).

W. H. G.

*p*-Nitrobenzenediazonium Chloride. HANS T. BUCHERER (*Ber.*, 1909, 42, 1852—1853).—A reply to Schwalbe (this vol., i, 445).

C. H. D.

[1-Diazo-2-oxynaphthalene-3-carboxylic Acid and its Azo-derivatives.] BASLER CHEMISCHE FABRIK (D.R.-P. 206698).—Diazo-2-oxynaphthalene-3-carboxylic acid when introduced in paste form into alkaline solutions of  $\alpha$ - and  $\beta$ -naphthol, resorcinol, *m*-hydroxydiphenylamine, *m*-phenylenediamine, and other similarly reactive phenols and amines gives rise to azo-dyes, which are sufficiently soluble to dye wool and yield fast shades on chroming.

*Nitro-1-diazo-2-oxynaphthalene-3-carboxylic acid*, light yellow needles from methyl alcohol and ethyl acetate, m. p. 212—213°, is obtained by nitrating the foregoing diazoimide with a mixture of nitric and sulphuric acids at 0—5°; it gives rise to similar azo-dyes.

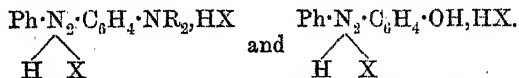
F. M. G. M.

Salts of Azobenzene, Amino- and Hydroxy-azo-compounds with Mineral Acids. ARTHUR HANTZSCH (*Ber.*, 1909, 42, 2129—2135. Compare Hantzsch and Hilscher, *Abstr.*, 1908, i, 484).—An optical examination of the salts of azobenzene, *p*-aminoazobenzene derivatives, and *p*-hydroxyazobenzene derivatives with mineral acids. It is shown that these salts belong to three widely different types:

(1) Yellow ammonium salts,  $\text{Ar} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2 \cdot \text{HX}$ , optically similar to azobenzene.



(2) Dark yellow azo-salts,  $\text{Ar} \cdot \text{N}_2 \cdot \text{Ar}$ . Solutions of azobenzene in indifferent solvents give a different absorption spectrum to solutions of this substance in strong acids. The absorption spectrum of the latter is similar to that of aminoazobenzene and hydroxyazobenzene derivatives in strong acids, so that these substances are present as salts having the formulæ:



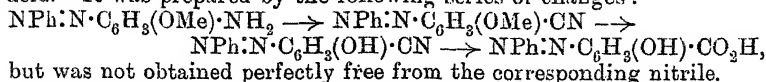
(3) Violet quinonoid salts,  $\text{Ar} \cdot \text{NH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2 \cdot \text{X}$ , the absorption spectrum of which is quite different from the spectra of the preceding salts.

A violet, crystalline *hydrobromide* of *p*-hydroxyazobenzene,  $\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \cdot \text{HBr}$ , has been prepared by passing hydrogen bromide into an ethereal solution of the azo-compound; it probably has the quinonoid oxonium formula:  $\text{Ph} \cdot \text{NH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{O} < \begin{array}{c} \text{H} \\ \text{Br} \end{array}$

W. H. G.

Benzeneazosalicylic Acid with the Carboxyl Group in the para-Position. HERMANN FINGER and E. WILNER (*J. pr. Chem.*, 1909, [ii], 79, 451—453).—An account of the preparation of the simplest

member of a class of important dyes, namely, *p*-benzeneazosalicylic acid. It was prepared by the following series of changes:



but was not obtained perfectly free from the corresponding nitrile.

Benzeneazo-*o*-anisidine, when diazotised and treated with potassium cuprous cyanide, yields 4-cyano-3-methoxy-1-azobenzene,  $\text{C}_{14}\text{H}_{11}\text{ON}_3$ , obtained as a mass of red needles having a characteristic odour. The latter substance is converted by treatment with aluminium chloride in carbon tetrachloride into 4-cyano-3-hydroxy-1-azobenzene,  $\text{C}_{13}\text{H}_9\text{ON}_3$ , which crystallises in small, reddish-yellow needles, and is not completely hydrolysed even by boiling with alcoholic potassium hydroxide for twenty hours; the *acid*, contaminated with some of the nitrile, was obtained as a deep red, crystalline substance. W. H. G.

**Influence of Proteins on the Solubility of Electrolytes.** WOLFGANG PAULI and MAX SAMEC (*Biochem. Zeitsch.*, 1909, 17, 235—256).—Solubility determinations were made at 25°, in flasks placed in an Ostwald thermostat with the usual precautions, of a number of salts in pure water, in ox-serum, purified from mineral salts by many weeks dialysis, and in 4% and 10% gelatin. The serum contained 2.23% protein and less than 0.005% ash.

Easily soluble salts, such as ammonium chloride, magnesium chloride, and ammonium thiocyanate, were less soluble in the protein solutions. Calcium sulphate is slightly more soluble in serum than in pure water, calcium phosphate and calcium carbonate relatively much more so, and silica and uric acid even more so. The least soluble salts showed proportionally the greatest increase in solubility. The same holds, although to a less extent, for solutions in 1.5% gelatin. Witte's peptone behaved somewhat differently; it contained 0.44% ash, and increased the solubility only of calcium carbonate, the other salts being slightly less soluble in it than in water. E. F. A.

**Hydrolysis of Serum-globulin by Alkalis.** H. LAMPFEL and ZDENKO H. SKRAUP (*Monatsh.*, 1909, 30, 363—375).—The hydrolysis of serum-globulin from horse blood by warm 6% sodium hydroxide is quite similar to that of egg-albumin (this vol., i, 340). The products being 11% of *globulin-protalbic acid*, precipitated by dilute sulphuric acid, 21% of *globulin-lysalytic acid*, precipitated by ammonium sulphate, and 6% of *globulin-peptone*, soluble in a solution of ammonium sulphate.

The three products and the original serum-globulin have been hydrolysed by 33% sulphuric acid; the table shows the results in parts %:

	Serum.	Protalbic acid.	Lysalytic acid.	Peptone.
Histidine .....	1.7	1.5	1.7	1.5
Arginine .....	3.7	0.0	0.0	0.0
Lysine .....	4.3	3.9	4.4	4.4
Tyrosine .....	3.1	4.4	2.5	1.2
Proline .....	3.0	3.2	2.9	2.3
Phenylalanine .....	3.6	1.0	2.7	1.8
Glutamic acid .....	4.4	—	1.9	0.0
Amino-acids .....	18.5	20.4	21.2	13.5

Colour reactions with  $\alpha$ -naphthol and thymol indicate that the carbohydrate content of the protalbic acid is very much smaller than that of the peptone.

C. S.

**The Relation of Different Acids to the Precipitation of Casein and to the Solubility of Cheese Curds in Salt Solution.** JOHN L. SAMMIS and EDWIN B. HART (*J. Biol. Chem.*, 1909, 6, 181—187. Compare Abstr., 1905, i, 498).—Experiments have been made by adding 0.1*N*-solutions of different acids to 10 c.c. of a 10% solution of casein in lime water, and observing in each case how much acid was required (1) to remove the red colour of the phenolphthalein indicator added; (2) to cause visible separation of a precipitate; (3) to cause complete flocculation of the precipitate; (4) to give a precipitate completely and readily soluble in 5% salt solution; (5) to give a precipitate quite soluble in the salt solution. The amount of acid required varies not merely with the acid used, but also with the temperature. The acids used were lactic, oxalic, acetic, and phosphoric. The age of the casein solution is also an important factor. The solubility of the precipitate in 5% salt solution changes completely when the precipitate is kept for a few minutes before decanting.

The solubility of cheese curd in 5% solutions of sodium, potassium, magnesium, ammonium, barium, and calcium chlorides has been determined. The curd is very sparingly soluble in barium and calcium chloride solutions, but readily soluble in sodium, potassium, and ammonium chloride solutions.

J. J. S.

**A Stable Derivative of Hæmochromogen.** The Carbon Monoxide Capacity of Reduced Acid Hæmatin. J. A. MILROY (*J. Physiol.*, 1909, 38, 384—391, 392—400).—When hæmatin dissolved in glacial acetic acid is reduced with aluminium in the presence of nickel acetate, a stable pigment is formed; this appears to be a derivative of hæmochromogen, in which nickel has largely replaced the iron. It is not altered by exposure to the air, and does not unite with carbon monoxide.

Reduced acid hæmatin is capable of uniting with carbon monoxide; its specific capacity for this gas is about 355—356 c.c. Some spectroscopic evidence is adduced for the view that the reduction of acid hæmatin takes place in two stages.

W. D. H.

**Preparation of Hæmatoporphyrin and other Blood Derivatives.** FRIEDRICH ESCHBAUM (*Ber. deut. pharm. Ges.*, 1909, 19, 284—292).—Hæmatoporphyrin may be prepared by adding 6 grams of goat's blood to 100 grams of sulphuric acid, heating until a clear solution is obtained, cooling, and pouring the mixture into three times its volume of alcohol. To this liquid enough of an alcoholic solution of potassium hydroxide is added to just neutralise the acid. The solution is then decanted from the precipitated potassium sulphate and evaporated to dryness. This preparation gives the characteristic spectra of hæmatoporphyrin in neutral, acid, or alkaline solution. Descriptions of the methods of preparing methæmoglobin, hæmatin, hæmochromogen, carbonylhæmoglobin, sulphohæmoglobin, and cyano-

hæmoglobin, and the behaviour of these substances with Stokes' reagent, and methods of recognising them are given.

The author is of opinion that the formation of sulphohæmoglobin does not take place in cloacal poisoning, since in his experience this substance cannot be detected in blood withdrawn from blood-vessels in such cases. Similarly, cyanohæmoglobin cannot be detected in the blood of dogs poisoned with hydrocyanic acid, nor can it be prepared by adding the acid to unchanged blood. Methæmoglobin is readily detected in blood withdrawn from the fingers of persons engaged in working with aniline or phenylhydrazine. T. A. H.

**The Pigment of Blood.** OSCAR PILOTY (*Annalen*, 1909, 366, 237—276. Compare Küster, Abstr., 1901, i, 298; 1902, i, 845; 1904, i, 357; Nencki and Zaleski, Abstr., 1901, i, 434; Zaleski, Abstr., 1903, i, 217).—An investigation of the degradation products of hæmatoporphyrin.

It has been found possible to obtain hæmopyrrole, one of the reduction products of hæmatoporphyrin, in a pure state, and also to isolate two other substances formed simultaneously with hæmopyrrole. One of these substances is designated hæmopyrrolecarboxylic acid, and has the formula  $\text{NH} \begin{matrix} \text{CH:CHMe} \\ \text{CH:C} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H} \end{matrix}$ ; the nature of the side-chain and its position in the pyrrole nucleus is, however, not yet definitely settled.

Hæmopyrrole and hæmopyrrolecarboxylic acid are derived from two distinct portions of the hæmatoporphyrin molecule, since the molecule of the compound remaining after the elimination of these substances contains either 14 or 17 carbon atoms. This compound, named provisionally hæmatopyrrolidinic acid, has not been isolated in a pure state, and analyses of its salts have not led to definite conclusions as to its chemical composition. However, when it is oxidised it yields a substance, which is probably a derivative of a hydropyrrole, and hæmopyrrolecarboxylic acid, which is further oxidised to hæmatic acid.

When hæmatoporphyrin is reduced gently with zinc and hydrochloric acid, it yields a pigment, named deoxyhæmatoporphyrin, which probably has the formula  $\text{C}_{34}\text{H}_{38}\text{O}_5\text{N}_4$ , and breaks down when treated with energetic reducing agents into hæmopyrrole, hæmopyrrolecarboxylic acid, and hæmatopyrrolidinic acid. The products of reduction just mentioned are rapidly acted on by atmospheric oxygen with the formation of various brown substances. It is extremely probable that Hoppe-Seyler's urobilin (Abstr., 1875, 96) is a mixture of these substances.

Hæmopyrrole is a colourless oil with a faint blue fluorescence, b. p.  $86-87^\circ/23$  mm. (compare Nencki and Zaleski, *loc. cit.*). It is converted by nitrous acid into two substances, one of which forms crystals, m. p.  $66^\circ$ , and is probably the *imide* of methylethylmaleic acid, whilst the other crystallises in almost colourless prisms, m. p.  $206-207^\circ$ , and is probably the *oxime*,  $\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2$ , of the former substance.

*Hæmopyrrolecarboxylic acid*,  $\text{C}_9\text{H}_{13}\text{O}_2\text{N}$ , crystallises in tufts of white, slender, pointed needles, m. p.  $125^\circ$ ; the *picrate*,  $\text{C}_{15}\text{H}_{16}\text{O}_9\text{N}_4$ , forms

yellow, prismatic leaflets, sinters at  $140^{\circ}$ , m. p.  $148^{\circ}$ ; the *methyl* ester,  $C_{10}H_{15}O_3N$ , crystallises in long, slender needles, m. p.  $56^{\circ}$ . An ethereal solution of the acid, when exposed to the action of dry air, deposits a *substance*,  $C_{18}H_{24}O_4N_2$  (?), obtained as a brownish-red powder, a solution of which in alcohol quickly changes from brown to green when exposed to the air. Another *substance*,  $C_{18}H_{22}O_4N_2$ , obtained as a violet powder, was isolated from a mixture of coloured substances obtained by the prolonged action of the air on an ethereal solution of the acid. Nitrous acid acts on hæmopyrrolecarboxylic acid, yielding hæmatic acid and a substance which is probably the *oxime*,  $C_8H_{10}O_4N_2$ , of hæmatic acid; it crystallises in colourless leaflets, commences to sinter at  $221^{\circ}$ , m. p.  $243^{\circ}$  (decomp.).

*Deoxyhaematoporphyrin*,  $C_{34}H_{38}O_5N_4$ , is an amorphous, granular, brown powder. An isomeric *substance*,  $C_{34}H_{38}O_5N_4$ , is obtained as a blue powder by reducing hæmatoporphyrin with zinc dust and glacial acetic acid.

*Haematopyrrolidinic acid* could not be crystallised; the *picrate*,  $(C_{17}H_{28}O_2N_2)_2 \cdot (C_6H_3O_7N_3)_3$  or  $C_{14}H_{22}O_2N_2 \cdot C_6H_3O_7N_3$ , is a lemon-yellow, amorphous powder, which commences to carbonise at  $125^{\circ}$ . The acid when oxidised with manganese dioxide and sulphuric acid yields hæmatic acid and a *substance*, obtained as a colourless oil, having an odour like piperidine; the *picrate* is an amorphous powder.

W. H. G.

**Inosic Acid. III.** PHCEBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 1198—1203. Compare this vol., i, 164; Haiser and Wenzel, *Abstr.*, 1908, i, 561).—The authors have finally succeeded in obtaining the pentose derived from inosine in a crystalline condition, and have in consequence been enabled to support their contention that it is neither *l*-xylose, as stated by Neuburg and Brahn (*Abstr.*, 1908, i, 1029), nor *r*-arabinose, as argued by Bauer (*Abstr.*, 1907, i, 1098). It is probably either *d*-ribose or *d*-arabinoketose.

The pentose was prepared from carnine by the method of Haiser and Wenzel (*loc. cit.*), and crystallised from hot absolute alcohol. It forms microscopic plates, m. p.  $86-87^{\circ}$  (corr.),  $[\alpha]_D -19.5^{\circ}$  in water. A solution of 0.1006 gram of the phenylosazone in 5 c.c. of pyridine alcohol gave  $\alpha_D 1.16^{\circ}$  in a 1-dcm. tube. The *phenylbenzylhydrazones*,  $C_{18}H_{22}O_4N_2$ , has m. p.  $127-128^{\circ}$  (corr.),  $[\alpha]_D -26.46^{\circ}$  in alcohol.

W. H. G.

**Carnine and Inosic Acid. III.** FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1909, 30, 377—386. Compare this vol., i, 322).—The pentose obtained from inosine has definitely been identified with *d*-lyxose by the comparison of the *phenylbenzylhydrazones*, m. p.  $127^{\circ}$  and  $128^{\circ}$  respectively.

The molecular formula of inosic acid is proved to be  $C_{10}H_{13}O_8N_4P$  in two ways. The increase of the equivalent conductivity of the sodium salt between the dilutions 32 and 1024 shows that inosic acid is dibasic. The molecular weight by the cryoscopic method of inosic acid in aqueous solution has been found in two experiments to be 256.8 and 273.5; applying the correction for ionic dissociation, determined from

the relation  $\alpha = \mu/\mu_\alpha$ , the preceding values become 350.9 and 362.9, the theoretical value being 348. C. S.

**Inosic Acid.** CARL NEUBERG and R. BRAHN (*Biochem. Zeitsch.*, 1909, 17, 293—296. Compare Abstr., 1908, i, 1029; Hauser and Wenzel, this vol., i, 322).—Polemical. The authors uphold the view that the sugar obtained on hydrolysing inosic acid is *L*-xylose. E. F. A.

**The Pentose in Nucleic Acids.** PHOEBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 2102—2106).—The pentose obtained from inosic acid (compare preceding abstracts), which it is proposed to designate provisionally *carnose*, is in all probability also present in guanylic acid obtained from the liver and the pancreas, likewise in the nucleic acid from yeast; at least, the osazone of the sugar obtained from each acid has the same properties. It is further shown that *carnose* is not *D*-lyxose, as suggested by Hauser and Wenzel (this vol., i, 322), since lyxose yields a xylosazone quite different from the osazone of *carnose*.

The following derivatives of *carnose* have been prepared: *phenylhydrazone*, long, silky needles, m. p. 124—127°,  $[\alpha]_D^{20} + 4.53^\circ$  (in alcohol); *p*-*bromophenylhydrazone*, colourless, silky needles, which sinter at 168°, m. p. 172—173° (decomp., corr.),  $[\alpha]_D^{20} - 5.69^\circ$  (in alcohol). W. H. G.

**Yeast Nucleic Acid.** PHOEBUS A. LEVENE (*Biochem. Zeitsch.*, 1909, 17, 120—131).—Yeast nucleic acid was obtained as a snow-white powder,  $[\alpha]_D$  about  $+36^\circ$  in 10% ammonia, having the composition  $C_{88}H_{50}O_{25}N_{15}P_4$ . It yields about 20% of its weight as bases, consisting of adenine, guanine, uracil, and cytosine, present in equimolecular quantities. The only carbohydrate present is a pentose, of which the nature has not been identified. On alkaline hydrolysis, phosphoric acid is eliminated, but no reducing substance obtained; complexes of sugar and base are formed of glucosidic character, which are resistant towards alkalis, but easily hydrolysed by acids. By partial hydrolysis with dilute sulphuric acid, a complex, consisting of phosphoric acid-pentose-uracil, was obtained. E. F. A.

**Hydrolysis of Proteins by Acids.** HENRI MATHIEU (*Compt. rend.*, 1909, 148, 1218—1221).—The hydrolysis of gelatin has been effected by sulphuric, hydrochloric, and oxalic acids, and Siegfried's coefficient,  $N/CO_2$ , determined from time to time in the product (Abstr., 1908, i, 379). By plotting the value of this coefficient against the time, a characteristic discontinuous curve is obtained. This throws light on the course of hydrolysis by facilitating the determination of the successive stages at which the various amino-acids are produced. W. O. W.

**Soluble Chitin.** CARL L. ALSBERG and C. HEDBLÖM (*Proc. Amer. Soc. Biol. Chem.*, 1908, xlv; *J. Biol. Chem.*, 6).—Chitin from *Limulus* resembles other chitins in composition. If treated with 10% hydro-

chloric acid at room temperature for nine months, it gelatinises and forms a colloidal solution. The colloidal material loses its power of being coloured by iodine. The solutions are irreversible. Soluble chitin does not reduce Fehling's solution; its percentage of oxygen is increased; it dialyses very slowly.

W. D. H.

**Action of Alkalis on Protein.** I. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1909, 59, 492—498).—When protamines, for example, clupeine, are left in contact with 0.5*N*-sodium hydroxide solution at the ordinary temperature, a diminution of the laevorotation is observed, for example, from  $-2.6^{\circ}$  to  $0.5^{\circ}$  at the end of seven days. This is probably due to a process of racemisation, since the product when hydrolysed by acids yields *dl*-arginine, whereas clupeine itself yields an active arginine. By the prolonged action of barium hydroxide solution on clupeine at  $40^{\circ}$ , *dl*-ornithine is obtained. Experiments have shown that *d*-ornithine and *d*-arginine themselves are not racemised by the action of alkalis, so that the arginine groups appear to be more reactive towards racemising agents when present as part of a protein molecule.

Some of the higher proteins, for example, gelatin, react with alkalis in much the same manner as clupeine. The ornithine was isolated as the sulphate,  $2C_5H_{12}O_2N_2 \cdot H_2SO_4$ , m. p.  $213^{\circ}$ .

J. J. S.

**Action of Alkalis on Proteins.** II. ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1909, 60, 311—316. Compare preceding abstract).—By the action of 0.5*N*-sodium hydroxide solution on clupeine, a clupeone is obtained, which can be precipitated by the silver sulphate-baryta method. The product differs from the clupeone obtained by the action of dilute acids on clupeine; for example, it yields less arginine, but more amino-acids, and when completely hydrolysed by acids the alkali-clupeone yields a substance which is precipitated by phosphotungstic acid, but not by the silver-baryta process.

The alkali-clupeone does not contain free ornithine, but when hydrolysed by dilute acids yields *dl*-ornithine. The formation of this product is regarded as further evidence in favour of the view that alkali produces racemisation in the protein molecule.

J. J. S.

**Salts of Inactive Ornithine.** FR. WEISS (*Zeitsch. physiol. Chem.*, 1909, 59, 499—505. Compare E. Fischer, *Abstr.*, 1901, i, 192; Riesser, *ibid.*, 1907, i, 77; Ackermann, 1908, i, 774).—*dl*-Ornithine was prepared by the action of barium hydroxide solution on clupeine (compare preceding abstracts). The nitrate,  $C_5H_{12}O_2N_2 \cdot HNO_3$ , is deposited as crystalline needles from aqueous alcohol, and has m. p.  $183^{\circ}$ . The hydrochloride,  $C_5H_{12}O_2N_2 \cdot HCl$ , forms slender needles, m. p.  $215^{\circ}$ . The oxalate,  $2C_5H_{12}O_2N_2 \cdot H_2C_2O_4$ , forms crystalline plates, m. p.  $218^{\circ}$ . The picrate,  $C_5H_{12}O_2N_2 \cdot C_6H_3O_7N_3$ , does not contain water of crystallisation, and has m. p.  $195^{\circ}$  (Riesser gives  $170^{\circ}$ ). The picrolonate,  $C_5H_{12}O_2N_2 \cdot C_{10}H_8O_5N_4 \cdot 1.5H_2O$ , forms long, yellow needles, m. p.  $220-221^{\circ}$  (decomp.). The acetate,  $C_5H_{12}O_2N_2 \cdot C_2H_4O_2$ ,

is not so characteristic as the acetate of *d*-ornithine. It forms plates, m. p. 163—164°, and is readily soluble.

The compounds  $2\text{C}_5\text{H}_{13}\text{O}_2\text{N}_2\cdot\text{CuSO}_4\cdot\text{H}_2\text{O}$ , m. p. 204—205° (decomp.),  $2\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2\cdot\text{Cu}(\text{NO}_3)_2\cdot\frac{1}{2}\text{H}_2\text{O}$ , m. p. 167—168°, and

$\text{C}_5\text{H}_{12}\text{O}_2\text{N}_2\cdot\text{HNO}_3\cdot\text{AgNO}_3$ , which darkens at 130°, have been prepared.

J. J. S.

**Inhibition and Reactivation of Enzyme Action by Mercuric Chloride.** S. HATA (*Biochem. Zeitsch.*, 1909, 17, 156—187).—Mercuric chloride inhibits the action of pepsin, trypsin, rennet, ptyalin, the proteolytic enzyme of the liver, and enzymes which decompose hydrogen peroxide. The opposite action was never observed. The action of the enzymes is, however, restored by agents which precipitate mercury from solution. The enzymes are precipitated by mercuric chloride with greater difficulty than the proteins which accompany them; this may be used to separate enzymes from protein, and they may then be reactivated by precipitating the mercury with potassium sulphide.

W. D. H.

**Influence of Reaction of the Medium on the Activity of Maltases from Maize.** R. HUERRE (*Compt. rend.*, 1909, 148, 1121—1123. Compare this vol., ii, 258, 338).—Variation of the reaction of the solution by addition of sulphuric acid or potassium hydroxide has considerable influence on the action of the enzymes in maize extract. Some species of maize contain maltases which only exert their maximum activity in an alkaline solution, whilst others require a neutral or feebly acid medium. The author's experiments confirm his previous conclusions as to the plurality of maltases in maize.

W. O. W.

**Chemistry of the Higher Fungi. III. Fungus Diastase.** JULIUS ZELLNER (*Monatsh.*, 1909, 30, 231—246. Compare Abstr., 1909, ii, 175).—Amylolytic enzymes are widely distributed in fungi which grow on wood, and remain active for a prolonged period in the dried fungi. The ferment activity is easily impaired by dilute inorganic acids and bases; dilute organic acids have an accelerating influence. The diastatic action is most rapid at 40—60°, the optimum temperature being at about 50°; the ferment is destroyed at 70°. The diastatic power of fungi is relatively small in comparison with that of barley malt. The products of action are at first dextrins, and finally dextrins and dextrose; maltose if formed is probably destroyed by maltases in the fungus sap. The fungus enzyme is without action on inulin and arabin.

E. F. A.

***p*-Iodophenylarsinic Acid and Arsenious *p*-Iodophenyl Iodide.** EFISIO MAMELI and A. PATTÀ (*Boll. Soc. Med.-Chirurg. Pavia*, 1909).—Substitution of the amino-group of *p*-aminophenylarsinic acid (compare Ehrlich and Bertheim, Abstr., 1907, i, 812) by iodine by Sandmeyer's reaction leads to the formation of various compounds, of which the authors here describe the following.

*p*-Iodophenylarsinic acid,  $C_6H_4I \cdot AsO(OH)_2$ , is an infusible substance, crystallising from alcohol, acetone, or acetic acid in shining, white needles and exhibiting the characteristic reactions of the phenylarsinic acids.

Arsenious *p*-iodophenyl iodide,  $C_6H_4I \cdot AsI_2$ , which can also be obtained directly from *p*-iodophenylarsinic acid by heating for a short time or by prolonged contact with concentrated hydriodic acid, crystallises from acetic acid in golden-yellow needles or scales, m. p.  $80^\circ$ .

The therapeutic uses of these two products and of the others obtained are being investigated. T. H. P.

**Magnesium Derivatives of Xylyl Bromides.** PAUL CARRÉ (*Compt. rend.*, 1909, 148, 1108—1110; *Bull. Soc. chim.*, 1909, [iv], 5, 486—489. Compare Tiffeneau, *Abstr.*, 1903, i, 819; 1904, i, 48).—The chief product formed when magnesium acts on an ethereal solution of a xylyl bromide is the corresponding dimethyldibenzyl (Moritz, *Abstr.*, 1899, i, 910); only a small quantity of the organo-magnesium compound is formed. Magnesium *m*-xylyl bromide reacts with formaldehyde giving Kling's *m*-tolylethyl alcohol, b. p.  $112-113^\circ/10$  mm. (*Abstr.*, 1908, i, 980); its *acetyl* derivative has b. p.  $115-116^\circ/18$  mm. The following alcohols have been prepared in the same way: *m*-Tolylisopropyl alcohol,  $C_7H_7 \cdot CH_2 \cdot CHMe \cdot OH$ , b. p.  $119-120^\circ/18$  mm. Its *acetyl* derivative has b. p.  $116-117^\circ/20$  mm.; the benzoyl derivative has b. p.  $188-190^\circ/12$  mm. *m*-Tolyl-tert.-butyl alcohol,  $C_7H_7 \cdot CH_2 \cdot CMe_2 \cdot OH$ , b. p.  $107-108^\circ/10$  mm., has an odour resembling that of terpineol; its *acetyl* derivative has b. p.  $119-120^\circ/16$  mm. *o*-Tolyl-tert.-butyl alcohol has b. p.  $125-126^\circ/22$  mm. W. O. W.

**Action of Magnesium Phenyl Bromide on Styrene.** EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1908, [iii], 14, 245—248).—When cinchonine (cinchotoxine) (1 mol.) is treated with magnesium phenyl bromide (4 mols.) in ethereal solution, the ether, when distilled off, is found to be accompanied by an amount of benzene corresponding with about 1 mol. of magnesium phenyl bromide; similarly, when magnesium  $\alpha$ -naphthyl bromide is used, a corresponding amount of naphthalene distils over. The vinyl group of the cinchonidine evidently reacts with the organo-magnesium compound in the same way as does acetylene (compare Oddo, *Abstr.*, 1907, i, 549):  $CHR:CH_2 + MgPhBr = CHR:CH \cdot MgBr + C_6H_6$  and  $CHR:CH_2 + Mg(C_{10}H_7)Br = CHR:CH \cdot MgBr + C_{10}H_8$ .

This reaction is not confined to complex compounds containing a vinyl group, since with magnesium phenyl bromide and styrene, benzene is obtained. T. H. P.

## Organic Chemistry.

**Preparation of Hydrocarbons by Electrolytic Reduction of Acetoacetic Esters.** JULIUS TAFEL and WILHELM JÜRGENS (*Ber.*, 1909, 42, 2548—2556).—It was shown by Tafel and Hahl (*Abstr.*, 1907, i, 765) that  $\beta$ -benzylbutane is obtained by the electrolytic reduction of ethyl benzylacetoacetate, and it is now found that the reaction may be extended to ethyl acetoacetate and its substituted derivatives, only failing in the case of ethyl diacetylsuccinate, which is reduced to ethyl diethylsuccinate, no hydrocarbon being produced.

Aqueous-alcoholic sulphuric acid is used as solvent, and a lead cylinder as cathode, enclosed in a porcelain cell with gas-tight lead cap and condenser. A high current density (up to 0.76 ampere per sq. dm.) and high temperature are necessary. The current concentration is from 100 to 500 amperes per litre of cathode solution. The products are purified by fractional distillation.

Ethyl acetoacetate yields butane.  $\gamma$ -Methylhexane, from ethyl propylacetoacetate, has b. p. 98—99°/748 mm.,  $D_4^{19}$  0.684 (compare Welt, *Abstr.*, 1895, ii, 97); ethyl butylacetoacetate yields  $\gamma$ -methylheptane; ethyl isobutylacetoacetate yields  $\beta\delta$ -dimethylhexane, b. p. 117—118°/751 mm.,  $D_4^{19}$  0.698 (compare Clarke, *Abstr.*, 1908, i, 593).  $\gamma$ -Methyl- $\gamma$ -ethylpentane, from ethyl diethylacetoacetate, has b. p. 118.5—119°/750 mm.,  $D_4^{19}$  0.713,  $n_D^{19}$  1.4028.  $\beta$ -Benzylbutane has b. p. 203—204°/750 mm.,  $D_4^{19}$  0.860 (compare Tafel and Hahl, *loc. cit.*).  $\beta$ -Benzyl- $\beta$ -methylbutane, from ethyl benzylmethylacetoacetate, has b. p. 214.5°/753 mm.,  $D_4^{19}$  0.860,  $n_D^{19}$  1.4882. C. H. D.

**Catalytic Actions of Colloidal Metals of the Platinum Group. VII. The Reduction of Ethylene.** CARL PAAL and WILHELM HARTMANN (*Ber.*, 1909, 42, 2239—2244. Compare *Abstr.*, 1908, i, 599; this vol., i, 358, 381).—On shaking ethylene and hydrogen together with palladium hydrosol, reduction of the ethylene to ethane takes place quantitatively. C. H. D.

***n*-Butinene and Some of its Derivatives.** GEORGES DUPONT (*Compt. rend.*, 1909, 148, 1522—1524. Compare Bruylants, *Ber.*, 1875, 3, 412).— $\beta\beta$ -Dichlorobutane has b. p. 102—104°, m. p. —74°,  $n_D$  1.4295.  $\beta$ -Chloro- $\Delta^{\alpha}$ -butylene has b. p. 61—62°,  $n_D$  1.4168.

$n$ - $\Delta^{\alpha}$ -Butinene (ethylacetylene), obtained with difficulty by Bruylant's process, is prepared by the following method with good yields. The vapour of *n*-butyl alcohol is passed over heated alumina (Senderens, *Abstr.*, 1908, i, 494), and the butylene absorbed by bromine. The butylene dibromide is then allowed to react at 180° with dry potassium hydroxide moistened with alcohol. Details are given for the preparation of *n*-butyl alcohol by a modification of Grignard's method.

$n$ - $\Delta^{\alpha}$ -Butinene is a liquid, b. p. 18.5°; m. p. —130°,  $D_0$  0.668,  $n_D$  1.3962 (compare Wislicenus, *Abstr.*, 1901, i, 2). With bromine

it forms the dibromide,  $\text{CBrEt}\cdot\text{CHBr}$ , b. p.  $150^\circ$ , m. p.  $-49.5^\circ$ ,  $D_0^{20}$  1.887, and a tetrabromide, which sublimes at  $200^\circ$  (compare Caventou, *Annalen*, 1863, 127, 93). The copper derivative when treated with iodine yields  $\alpha\alpha\beta$ -tri-iodo- $\Delta^2$ -butylene,  $\text{CI}\cdot\text{Et}\cdot\text{Cl}_2$ , m. p.  $26^\circ$ . When oxidised with potassium ferricyanide, it yields octadi-inene,  $\text{C}\cdot\text{Et}\cdot\text{C}\cdot\text{C}\cdot\text{Et}$ , a pale yellow liquid, b. p.  $163-164^\circ$ ,  $D_0^{20}$  0.826,  $n_D^{20}$  1.4968. When this is heated with alcoholic mercuric chloride, it forms *octan-ye-dione*,  $\text{COEt}\cdot\text{CH}_2\cdot(\text{O})\text{Pr}^2$ , characterised by a copper derivative, m. p.  $158.5^\circ$ .

Carbon dioxide reacts with butinene magnesium bromide, forming *n*-butinene- $\alpha$ -carboxylic acid; the *ethyl* ester has b. p.  $67-68^\circ/18$  mm.,  $D_0^{20}$  0.962, and forms a compound with piperidine,  $\text{C}_{12}\text{H}_{21}\text{O}_2\text{N}$ , b. p.  $165-166^\circ/17$  mm.,  $n_D^{20}$  1.5246; by hydrolysis of the latter, ethyl propionylacetate is obtained.

$\alpha$ -Phenyl  $\Delta^2$ -pentinene- $\alpha$ -ol,  $\text{OH}\cdot\text{CHPh}\cdot\text{C}\cdot\text{Et}$ , b. p.  $137-138^\circ/16$  mm.,  $D_0^{20}$  1.037,  $n_D^{20}$  1.5455, is prepared by the action of benzaldehyde on the above magnesium compound; its *benzoyl* derivative has m. p.  $59^\circ$ . It forms a *di-iodide*,  $\text{C}\cdot\text{Et}\cdot\text{I}\cdot\text{Cl}\cdot\text{CH}\cdot\text{Et}\cdot\text{OH}$ , m. p.  $196^\circ$ . When acetone reacts with butinene magnesium bromide, *a*-methyl- $\Delta^2$ -hexinen- $\beta$ -ol,  $\text{CHMe}_2\text{OH}\cdot\text{C}\cdot\text{Et}$ , is formed. This has b. p.  $145-147^\circ$ ,  $D_0^{20}$  0.962,  $n_D^{20}$  1.4411. W. O. W.

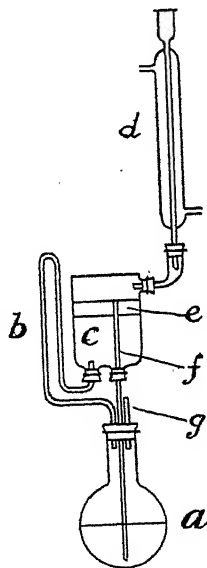
**Action of Metallic Oxides on Methyl Alcohol.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1909, 148, 1734-1736. Compare Abstr., 1908, i, 594, 713; Senderens, this vol., i, 127).—Methyl alcohol is less readily decomposed by finely divided copper than other primary alcohols; formaldehyde is produced at  $280^\circ$ , but at  $360^\circ$  complete decomposition into hydrogen and carbon monoxide occurs. Chromic oxide and tungsten dioxide at  $300^\circ$  give a mixture of methyl ether and formaldehyde with some hydrogen and carbon monoxide. With the oxides of glucinum, zirconium, zinc, uranium, molybdenum, vanadium, lead, tin, cadmium, and ferric oxide, the predominating action in one of dehydrogenation, with further decomposition of the formaldehyde so produced. The action is most rapid in the case of stannic oxide, but the velocity of reaction depends, in each case, on the method of preparation of the oxide. W. O. W.

**Action of Some Organo-magnesium Compounds on  $\alpha$ -Methylpentan- $\delta$ -one.** F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1909, 148, 1675-1677).—The reaction between organo-magnesium compounds and  $\alpha$ -methylpentan- $\delta$ -one is accompanied by the liberation of a saturated hydrocarbon corresponding with the magnesium derivative employed. Treatment of the product with hydrogen chloride yields a complex mixture containing a tertiary alcohol and the corresponding ethylenic hydrocarbon, with compounds of indefinite b. p. and much unaltered ketone. Magnesium ethyl iodide forms  $\beta\delta$ -dimethylhexan- $\delta$ -ol,  $\text{CH}_2\text{Pr}^2\cdot\text{CMeEt}\cdot\text{OH}$ , b. p.  $151-153^\circ/750$  mm.,  $D^{15}_{20}$  0.830,  $n_D^{18}$  1.4286. The following new compounds are also mentioned:  $\beta\delta$ -dimethylheptan- $\delta$ -ol,  $\text{CH}_2\text{Pr}^2\cdot\text{CMePr}^2\cdot\text{OH}$ , b. p.  $170-171^\circ/750$  mm.,  $D^{20}_{20}$  0.826,  $n_D^{18}$  1.4318;  $\beta\delta\zeta$ -trimethylheptan- $\delta$ -ol,  $\text{OH}\cdot\text{CMe}(\text{CH}_2\text{Pr}^2)_2$ , b. p.  $180-182^\circ/753$  mm.,  $D^{21}_{20}$  0.823,  $n_D^{18}$  1.4334. Phenyl magnesium bromide gives (1)  $\beta$ -phenyl- $\gamma$ -methylpentan- $\beta$ -ol,  $\text{CHMeEt}\cdot\text{CMePh}\cdot\text{OH}$ , b. p.  $125-128^\circ/18$  mm.,  $D^{18}_{20}$  0.952,  $n_D^{18}$  1.5157; (2)  $\beta$ -phenyl-

$\delta$ -methyl- $\Delta^8$ -pentene,  $\text{CHPr}^\beta\text{:CMePh}$ , b. p. 216—220°/738 mm., 111—115°/18 mm.,  $D_4^{16}$  0.909,  $n_D^{16}$  1.5231; (3)  $\delta$ -dimethyl- $\Delta^8$ -hepten- $\delta$ -ol,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CMe(OH)}\cdot\text{CH}_2\text{Pr}^\beta$ , b. p. 180—182°/753 mm.,  $D_4^{21}$  0.823,  $n_D^{19}$  1.4443; this compound has also been obtained, together with propylene, by treating an ethereal solution of allyl bromide and methylpentanone with magnesium. W. O. W.

**Action of Organo-magnesium Compounds on  $\beta$ -Hydroxy- $\alpha$ -methylbutaldehyde.** PAUL ABELMANN (*Ber.*, 1909, 42, 2500—2505).—The interaction of magnesium methyl iodide (2 mols.) and  $\beta$ -hydroxy- $\alpha$ -methylbutaldehyde leads to the formation of  $\gamma$ -methylpentan- $\beta\delta$ -diol,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$ , b. p. 104—105°/12.5 mm. (diacetate, b. p. 107—109°/19 mm.); when an excess of magnesium methyl iodide ( $2\frac{1}{4}$  mols.) is used, the product is contaminated with  $\beta$ -methylbutane- $\alpha\gamma$ -diol, obtained by the reduction of the original aldehyde. In a similar manner  $\beta$ -hydroxy- $\alpha$ -methylbutaldehyde reacts with magnesium ethyl bromide to form ultimately  $\gamma$ -methylhexane- $\beta\delta$ -diol,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHEt}\cdot\text{OH}$ , b. p. 112—113°/10 mm. (diacetate, b. p. 103—105°/10 mm.), and with magnesium propyl bromide to form  $\gamma$ -methylheptane- $\beta\delta$ -diol,  $\text{OH}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CHPr}^\alpha\cdot\text{OH}$ , b. p. 122—123°/15.5 mm. (diacetate, b. p. 113—114°/10 mm.). C. S.

**Ether Purifying and Extraction Apparatus.** RODOLFO FRITSCH (*Chem. Zeit.*, 1909, 33, 759—760).—The apparatus described enables large quantities of ether to be purified from alcohol in an expeditious and economical manner. In the accompanying figure, *a* represents a flask containing ether, which is heated to boiling on a water-bath; the vapour passes through tube *b* to the inverted Woulffe bottle containing a solution of calcium chloride, *c*, through which it passes, becoming partially condensed—any escaping vapour being condensed in *d*. A layer of ether, *e*, accumulates on the surface of *c*, and is automatically returned to *a* by a siphon, indicated by tube *f*. When once set in operation this purifying process becomes continuous and requires little attention; care must, however, be taken when completed, and the source of heat removed, to open the side-tube *g* at once, so as to prevent the calcium chloride solution entering the flask by tube *b*. It will be readily seen that this apparatus is also suitable for extraction purposes, the liquid to be extracted by ether taking the place of the calcium chloride solution. J. V. E.



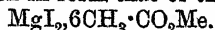
**The Nitrogenous Radicle of Lecithin and other Phosphatides.** HUGH MACLEAN (*Bio-Chem. J.*, 1909, 4, 240—257).—Further work is recorded which confirms the author's previous con-

clusion that choline is not the only nitrogen-containing group in lecithin; probably part of the nitrogen is in the form of amino-acid. The usually accepted formula for lecithin cannot therefore be correct. Lecithins from various sources, although often giving similar results on elementary analysis, differ in the amount of choline they yield.

W. D. H.

**The Solubility of the Molecular Compounds of Magnesium Bromide and Iodide in the Organic Compounds from which They are Formed.** BORIS N. MENSCHUTKIN (*Zeitsch. anorg. Chem.*, 1909, 62, 395—404. Compare Abstr., 1907, i, 19, 395; this vol., i, 82, 89).—The solubility curves obtained in the author's investigations are compared and plotted uniformly. They may be grouped in four classes, which, however, are not sharply distinguished.

The more stable the compound of the magnesium salt with an organic compound is, the more nearly its solubility curve resembles that of the hexahydrate in water. The solubility curves of the less stable compounds approach in form that of the compound



The order in which the organic compounds arrange themselves resembles that found by Walden (Abstr., 1906, ii, 527) for the solubility of metallic iodides and quaternary ammonium iodides in organic solvents, but is quite different from that obtained by Étard (Abstr., 1894, ii, 443) from solubility measurements of mercuric chloride.

C. H. D.

**Theory of Hydrolysis of Fats and Oils.** J. KELLNER (*Chem. Zeit.*, 1909, 33, 661—662. Compare this vol., i, 357).—The hydrolysis of fats by means of Twitchell's reagent, like the autoclave process, is to some extent a bi- and ter-molecular reaction, although the formation of the mono- and di-glycerides does not occur to the same extent as in the latter process.

The hydrolysis by means of the ferment of castor-oil seeds also gives rise to the formation of mono- and di-glycerides, although to a still less extent.

L. DE K.

**Glycerol Esters of Stearolic and Behenolic Acids.** H. QUENSELL (*Ber.*, 1909, 42, 2440—2452).—The existence in nature of glycerides of acids containing a triple linking has not yet been firmly established; compounds of this type have now been synthesised for the first time; they readily form additive compounds with one molecular proportion of chlorine or bromine, but react with two molecular proportions only on prolonged exposure in sunlight; they, however, never react with more than one molecule of iodine. Similarly they only add on one molecule of iodine chloride for each acid radicle they contain.

*Glycerol  $\alpha$ -monostearolate*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_{17}\text{H}_{31}$ , prepared by heating together equal parts of stearolic acid and anhydrous glycerol for five hours at 160—170°, or by heating in an oil-bath a mixture of sodium stearolate and  $\alpha$ -monochlorohydrin in a stream of carbon dioxide, crystallises from alcohol in colourless leaflets, m. p. 40.5°.

*Glycerol aa'-distearolate*,  $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31})_2$ , by heating *aa'*-dichlorohydrin with excess of sodium stearolate in a sealed tube for eight hours at  $180^\circ$ , or by heating anhydrous glycerol with an excess of stearolic acid under a pressure of 12 mm. for eight hours at  $190^\circ$ , crystallises from alcohol; m. p.  $38\cdot5^\circ$ .

*Glycerol aβ-distearolate*,  $\begin{array}{c} \text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31} \\ | \\ \text{CH}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31} \\ | \\ \text{CH}_2\cdot\text{OH} \end{array}$ , by heating *aβ*-dibromo-

hydrin with an excess of sodium stearolate for six hours in a sealed tube at  $175^\circ$ , crystallises from light petroleum, and has m. p.  $40^\circ$ .

*Glyceryl tristearolate*,  $\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31})_3$ , by heating trichlorohydrin with a slight excess of sodium stearolate in a sealed tube at  $190\text{--}200^\circ$ , does not crystallise well; it separates from alcohol in aggregates, which retain a good deal of solvent, and was dried at  $60^\circ$  for analysis; it has m. p.  $29^\circ$ .

*Epistearolhydrin*,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} > \text{O} \\ | \\ \text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{31} \end{array}$ , by heating epichlorohydrin

with sodium stearolate for eight hours at  $160^\circ$ , crystallises from alcohol in small, colourless scales, m. p.  $36^\circ$ .

*Glycerol α-monobehenolate*,  $\text{C}_{25}\text{H}_{46}\text{O}_4$ , the constitution of which is similar to that of the corresponding stearyl derivative, was prepared by heating *α*-monochlorohydrin with sodium behenolate for six hours at  $160^\circ$ ; it crystallises from alcohol in colourless leaflets, m. p.  $50\cdot5^\circ$ .

*Glycerol aa'-dibehenolate*,  $\text{C}_{47}\text{H}_{84}\text{O}_5$ , by heating *aa'*-dichlorohydrin with sodium behenolate in a sealed tube for six hours at  $180^\circ$ , crystallises from light petroleum; m. p.  $42^\circ$ .

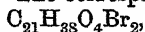
*Glycerol aβ-dibehenolate*,  $\text{C}_{47}\text{H}_{84}\text{O}_5$ , prepared as above from *aβ*-dibromohydrin, crystallises from alcohol, m. p.  $43^\circ$ .

*Glyceryl tribehenolate*,  $\text{C}_{69}\text{H}_{122}\text{O}_6$ , m. p.  $41^\circ$ , was obtained by heating trichlorohydrin with sodium behenolate in an atmosphere of carbon dioxide for ten hours at  $240^\circ$ , or by heating the acid with anhydrous glycerol under a pressure of 1 mm. for eighteen hours at  $205\text{--}210^\circ$ ; it separates from alcohol in colourless leaflets.

*Epibehenolhydrin*,  $\text{C}_{25}\text{H}_{44}\text{O}_3$ , by heating sodium behenolate with epichlorohydrin in a sealed tube for eight hours at  $180^\circ$ , crystallises from alcohol or light petroleum in colourless leaflets, m. p.  $43^\circ$ .

The iodine value of most of the above compounds was determined by Waller's modification of Hübl's method, and the *trichloriodide* of *glyceryl tribehenolate*,  $\text{C}_{69}\text{H}_{122}\text{O}_6\text{Cl}_3\text{I}_3$ , and *dichloriodide* of *glycerol dibehenolate*,  $\text{C}_{47}\text{H}_{84}\text{O}_5\text{Cl}_2\text{I}_2$ , were isolated and analysed.

*Glyceryl monostearolate dichloride*,  $\text{C}_{21}\text{H}_{38}\text{O}_4\text{Cl}_2$ , prepared by exposing to daylight a chloroform solution of a mixture of glycerol monostearolate with a slight excess over one molecular proportion of chlorine, forms a heavy oil. The corresponding *dibromide*,



obtained by the action of bromine in presence of iron filings or ferric chloride on monostearol glycerol in carbon disulphide solution, is a pleasant smelling, heavy oil.

The *di-iodide*,  $\text{C}_{21}\text{H}_{38}\text{O}_4\text{I}_2$ , prepared by the interaction of its

generators in carbon disulphide solution for four to five days in presence of ferrous or aluminium iodides, separates from alcohol in yellow aggregates, m. p.  $33^{\circ}$ .

The *tetrabromide*,  $C_{21}H_{38}O_4Br_4$ , produced by the action of two molecular proportions of bromide on the glycerol monostearolate for a week, is an unstable oil.

The *hexabromide* of glyceryl tristearolate,  $C_{57}H_{98}O_6Br_6$ , was also prepared.

*Glycerol monobehenolate dibromide*,  $C_{25}H_{46}O_4Br_2$ , prepared in carbon disulphide solution in presence of metallic iron, is a light-coloured oil; the corresponding *di-iodide*,  $C_{25}H_{46}O_4I_2$ , produced from its generators in the course of a week, is a thick oil, which solidifies on cooling.

*Glycerol dibehenolate tetrachloride*,  $C_{47}H_{84}O_5Cl_4$ , prepared in chloroform solution, is a thick oil.

P. H.

Synthesis of  $\beta$ -Ketonic Esters by means of Ethyl Diazoacetate. II. FRITZ SCHLOTTERBECK (*Ber.*, 1909, 42, 2565—2573. Compare Abstr., 1907, i, 676).—The synthesis of  $\beta$ -ketonic esters from aldehydes and ethyl diazoacetate is only possible when the aldehyde contains negative substituents. Ethyl diazopropionate or diazoacetophenone may also be used.

*Ethyl di- $\gamma$ -chloroacetoacetate*, from freshly prepared dichloroacetaldehyde, has b. p.  $203^{\circ}/761$  mm. *Ethyl  $\gamma$ -chloroacetoacetate*, from chloroacetaldehyde, has b. p.  $95^{\circ}/0.8$  mm.

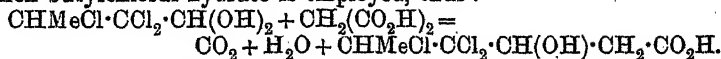
The chloro-esters obtained by Haller and Held (*Abstr.*, 1887, 799) and by Genvresse (*Abstr.*, 1889, 122) are not, as supposed,  $\gamma$ -derivatives, but  $\alpha$ -derivatives, as shown by Hantzsch (*Abstr.*, 1894, i, 171, 227); the above  $\gamma$ -chloro-esters are therefore new.

*Ethyl tri- $\gamma$ -bromoacetoacetate*,  $CBr_3 \cdot CO \cdot CH_2 \cdot CO_2Et$ , has b. p.  $158^{\circ}/14$  mm. *Ethyl  $\gamma\delta$ -dichloropropionylacetate*,  $CH_2Cl \cdot CHCl \cdot CO \cdot CH_2 \cdot CO_2Et$ , from  $\alpha\beta$ -dichloropropaldehyde, has b. p.  $38^{\circ}/0.2$  mm. *Ethyl  $\gamma\gamma\delta$ -trichlorobutyrylacetate*, from butyl chloral, has b. p.  $149^{\circ}/20$  mm.

Ethyl *p*-nitrobenzoylacetate is obtained from *p*-nitrobenzaldehyde with some difficulty, and is purified by conversion into the barium derivative and decomposition of this with sulphuric acid while suspended in ether.

C. H. D.

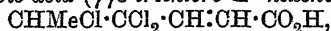
Condensation of Butylchloral and Butylchloral Hydrate with Malonic Acid. ADOLF RIEDEL and ERICH STRAUBE (*Annalen*, 1909, 367, 40—51).—The condensation of butylchloral with malonic acid proceeds in a manner analogous with that observed by von Garzarolli-Thurnlackh with chloral and malonic acid (compare Abstr., 1892, 429), in that carbon dioxide is eliminated with the formation of a  $\beta$ -hydroxycarboxylic acid. The reaction proceeds more smoothly when butylchloral hydrate is employed, thus:



$\gamma\delta$ -Trichloro- $\beta$ -hydroxy-*n*-hexoic acid,  $C_6H_9O_5Cl_3$ , prepared by heating butylchloral hydrate, malonic acid, and pyridine together on a water-bath and treating the product with dilute sulphuric acid, crystallises in large, hexagonal leaflets and long, rectangular prisms, m. p.  $102^{\circ}$ ;

the sodium salt ( $3\text{H}_2\text{O}$ ) forms long, white needles, m. p.  $91^\circ$ ; the methyl ester,  $\text{C}_8\text{H}_{11}\text{O}_3\text{Cl}_3$ , is a viscid, colourless oil with an aromatic odour, b. p.  $150^\circ/12$  mm.; the ethyl ester,  $\text{C}_8\text{H}_{13}\text{O}_3\text{Cl}_3$ , is a colourless oil, b. p.  $138^\circ/13$  mm., which slowly solidifies, forming large, four-sided leaflets.

*Trichlorohydroxosorbic acid* ( $\gamma\delta$ -trichloro- $\Delta^6$ -hexenoic acid),

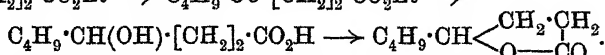
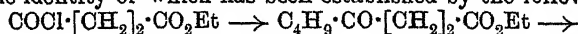


is prepared by treating anhydrous sodium  $\gamma\delta$ -trichloro- $\beta$ -hydroxy-*n*-hexoate with acetic anhydride; it crystallises in colourless needles, m. p.  $78^\circ$ ; the chloride,  $\text{C}_8\text{H}_9\text{OCl}_4$ , is a colourless liquid, b. p.  $109^\circ/10$  mm.; the amide,  $\text{C}_8\text{H}_7\text{ONCl}_3$ , crystallises in long, white needles, m. p.  $90^\circ$ ; the methyl ester,  $\text{C}_7\text{H}_9\text{O}_2\text{Cl}_3$ , is a colourless oil with a fruity odour, b. p.  $122^\circ/9$  mm.; the ethyl ester,  $\text{C}_8\text{H}_{11}\text{O}_2\text{Cl}_3$ , is a colourless oil, b. p.  $129^\circ/11$  mm. The acid is oxidised by potassium permanganate to  $\alpha\beta$ -trichlorobutyric acid, and reduced by sodium amalgam and water to *n*-hexoic acid. Treatment with zinc dust and dilute alcohol leads to the formation of  $\gamma$ -chlorosorbic acid,  $\text{CHMe}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , crystallising in long, white needles, m. p.  $116^\circ$ ; the ethyl ester,  $\text{C}_8\text{H}_{11}\text{O}_2\text{Cl}$ , is a colourless oil with a peppermint-like odour, b. p.  $138^\circ/13$  mm.; it solidifies in a freezing mixture, forming glistening leaflets.

W. H. G.

**Lactonisation of Acid Alcohols.** EDMOND É. BLAISE and A. KÖHLER (*Compt. rend.*, 1909, 148, 1772—1774).— $\xi$ -Lactones appear to be incapable of existence, since reactions which might be expected to result in their formation are accompanied by migration of the hydroxyl group. In order to ascertain the limit of lactone formation the following hydroxy-acids have been prepared by reducing the corresponding ketonic acids (this vol., i, 204) by means of zinc and potassium hydroxide in presence of platinum.

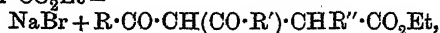
$\epsilon$ -Hydroxyoctanoic acid,  $\text{OH}\cdot\text{CHEt}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$ , is a viscous liquid which yields, on distillation in a vacuum,  $\epsilon$ -octolactone,  $\text{C}_8\text{H}_{14}\text{O}_2$ , b. p.  $114$ — $115^\circ/10$  mm.; sulphuric acid (50%) converts it into  $\gamma$ -*n*-octolactone, the identity of which has been established by the following synthesis:



$\xi$ -Hydroxynonanoic acid,  $\text{OH}\cdot\text{CHEt}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$ , has b. p.  $204^\circ/25$  mm., and does not form a lactone on distillation; sulphuric acid, however, converts it into  $\gamma$ -nonolactone,  $\text{C}_9\text{H}_{16}\text{O}_2$ , b. p.  $137$ — $138^\circ/14$  mm.

W. O. W.

**$\gamma\gamma'$ -Diketonic Acids.** JAMES B. GARNER, GUY A. REDDICK, and GAIL J. FINK (*J. Amer. Chem. Soc.*, 1909, 31, 667—669).—The sodium derivatives of  $\beta$ -diketones react with  $\alpha$ -brominated esters, best at temperatures near the b. p. of the ester, to form  $\gamma\gamma'$ -diketonic esters:  $\text{R}\cdot\text{CO}\cdot\text{CHNa}\cdot\text{CO}\cdot\text{R}' + \text{CHR}''\text{Br}\cdot\text{CO}_2\text{Et} =$



where  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Me}$  or  $\text{Ph}$ , and  $\text{R}'' = \text{H}$ ,  $\text{Me}$ , or  $\text{Et}$ . The resulting  $\gamma\gamma'$ -diketonic esters are yellow liquids, which develop intense colorations with ferric chloride, reduce gold, silver, and platinum salts, and form unstable monophenyldrazones, which readily lose water to form red,

viscous pyrazoles. All the esters respond to Knorr's pyrazoline reaction. The following new compounds have been prepared: *Ethyl*  $\beta\beta$ -diacetylpropionate,  $\text{CHAc}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $165^\circ/55$  mm.; *oxime*, m. p.  $120^\circ$ , and the *pyrazole*,  $\text{C}_{15}\text{H}_{18}\text{O}_2\text{N}_2$ , b. p.  $242^\circ/83$  mm. *Ethyl*  $\beta\beta$ -diacetyl- $\alpha$ -ethylpropionate,  $\text{CHAc}_2\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , b. p.  $205^\circ/27$  mm., and the *pyrazole*, b. p.  $237^\circ/45$  mm. *Ethyl*  $\beta\beta$ -diacetyl- $\alpha\alpha$ -dimethylpropionate,  $\text{CHAc}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $180^\circ/22$  mm., and the *pyrazole*,  $\text{C}_{17}\text{H}_{22}\text{O}_2\text{N}_2$ , b. p.  $215^\circ/20$  mm. *Ethyl*  $\beta$ -benzoyl- $\beta$ -acetylpropionate,  $\text{CHAcBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $194^\circ/44$  mm., forms a colourless, unstable phenylhydrazone, m. p.  $101$ — $106^\circ$ , which readily changes into the *pyrazole* derivative,  $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$ , b. p.  $270^\circ/47$  mm. *Ethyl*  $\beta$ -benzoyl- $\beta$ -acetyl- $\alpha$ -methylpropionate,  $\text{CHAcBz}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , b. p.  $205^\circ/69$  mm., and the *pyrazole*,  $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2$ , b. p.  $250$ — $253^\circ/55$  mm. *Ethyl*  $\beta$ -benzoyl- $\beta$ -acetyl- $\alpha$ -ethylpropionate,  $\text{CHAcBz}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , b. p.  $198^\circ/37$  mm., and the *pyrazole*,  $\text{C}_{20}\text{H}_{20}\text{O}_2\text{N}_2$ , b. p.  $250$ — $253^\circ/46$  mm. C. S.

**Digitoxonic and Digitalonic Acid.** HEINRICH KILIANI (*Ber.*, 1909, 42, 2610—2611).—Pure digitoxonic acid has been prepared through its crystalline phenylhydrazide with the object of determining whether it could be obtained in crystalline form; a syrupy residue, consisting for the most part of lactone, however, showed no signs of crystallisation after fourteen days. The *potassium*, *lead*, and especially *silver* salts were, however, found to be crystalline; the free acid liberated from the pure silver salt could not be made to crystallise, from which it appears that the phenylhydrazide still remains the only suitable derivative for the identification of this acid, with the possible exception of the silver salt, which forms stout, rhombic plates.

The lactone of digitalonic acid can be conveniently separated from gluconic acid (compare *Abstr.*, 1892, 1241) by shaking a syrupy mixture of the two substances with threetimes its volume of a mixture of one part of alcohol with four parts of ether; after allowing the precipitate to settle, the ethereal solution is siphoned off and allowed to evaporate spontaneously, when the pure lactone remains. The *phenylhydrazide* of digitalonic acid, obtained by mixing the lactone with phenylhydrazine in alcoholic solution, separates, after twenty-four hours, in the form of stout plates; it crystallises from a mixture of methyl alcohol with a large excess of absolute ether, and has m. p.  $174^\circ$ . P. H.

**Thionyltartaric Acid Esters.** EMIL SCHILLER (*Ber.*, 1909, 42, 2017—2020).—Ethyl tartrate and thionyl chloride in molecular quantities react at the ordinary temperature, or on warming to  $50^\circ$ , to form ethyl thionyltartrate,  $\text{SO} \begin{matrix} \diagup \text{O}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \diagdown \text{O}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \end{matrix}$ . This and corresponding esters are colourless, odourless, syrupy compounds, hydrolysed on long boiling with water, and are more easily volatile than the corresponding acid esters.

*Methyl thionyltartrate* has b. p.  $157.5^\circ/12.3$  mm.,  $274^\circ/770$  mm.,  $D_{19}^{20}$  1.4425,  $[\alpha]_D^{18}$   $-61^\circ$ .

*Ethyl thionyltartrate* has b. p.  $167^\circ/11.5$  mm.,  $279^\circ/770$  mm.,  $D_{19}^{20}$  1.3257,  $[\alpha]_D$   $-56.7^\circ$ .

*n*-Propyl thionyltartrate has b. p. 176°/12 mm., 295°/770 mm.,  $D_{19}^{19.5}$  1.2378,  $[\alpha]_D^{20}$  -18.5°.

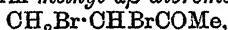
Methyl thionyltracetate has b. p. 158.5°/12.2 mm., 276°/770 mm.,  $D_{19}^{19.5}$  1.4648. E. F. A.

Conversion of Aldehydes into Ketones by Diazo-methane. II. FRITZ SCHLOTTERBECK (*Ber.*, 1909, 42, 2559—2564. Compare Abstr., 1907, i, 185).—The reaction previously described has been extended to negatively substituted aldehydes, and furnishes a means of obtaining substituted ketones not otherwise obtainable.

*Tri- $\alpha$ -chloroacetone*,  $\text{CCl}_3\cdot\text{COMe}$ , prepared by adding ethereal diazo-methane to chloral in absolute ether, cooling with a freezing mixture, forms a colourless, mobile liquid with somewhat sweet smell, b. p. 149°/764 mm. The trichloroacetone described in the literature is mainly the unsymmetrical compound.

By adding a further quantity of chloral in the above preparation, *s-trichloroacetonechloral*,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CCl}_3$ , may be obtained in white crystals, m. p. 88°.

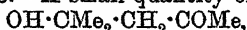
$\alpha\beta$ -Dibromopropionaldehyde, from acraldehyde and bromine, reacts with diazomethane to form *methyl  $\alpha\beta$ -dibromoethyl ketone*,



b. p. 53°/0.2 mm., a colourless oil with pleasant odour.

$\alpha\beta$ -Dichloropropaldehyde, b. p. 25°/0.2 mm., yields *methyl  $\alpha\beta$ -dichloroethyl ketone*,  $\text{CHCl}\cdot\text{CHCl}\cdot\text{COMe}$ , a colourless, mobile liquid, b. p. 30—40°/0.2 mm. C. H. D.

Condensation of Acetone by Calcium Oxide. ALFRED HOFFMAN (*J. Amer. Chem. Soc.*, 1909, 31, 722—724).—By boiling acetone in a Soxhlet apparatus containing calcium oxide in the extraction cup, a condensation product is obtained consisting almost entirely of mesityl oxide. A small quantity of diacetone,



is also formed, which becomes the sole product when calcium hydroxide is used as the condensing agent. Dry acetone and pure calcium oxide do not react at 105—110°, but in the presence of a trace of the hydroxide a viscous syrup of the higher condensation products is obtained. Calcium hydroxide and acetone give only a small quantity of diacetone. Dry mesityl oxide, alone or in the presence of acetone, reacts with calcium oxide only when the hydroxide is present.

The experiments show that the formation of mesityl oxide proceeds in two stages, and that the production of isophorone and the xylitones is due to the secondary condensation of mesityl oxide with acetone or with itself. C. S.

Products of the Reaction between Lactose and Calcium Hydroxide. HEINRICH KILIANI and FRITZ EISENLOHR (*Ber.*, 1909, 42, 2603—2610. Compare Abstr., 1908, i, 715).—The acid extract II (*loc. cit.*) has been examined once more, and found to contain isosaccharin. The dibasic acid,  $\text{C}_6\text{H}_{10}\text{O}_7$ , obtained from the oxidation products of extract IV is now proved to be a trihydroxyadipic acid

with a normal carbon chain, since it yields *n*-adipic acid on reduction with hydriodic acid and red phosphorus.

With the object of further characterising meta- and para-saccharin, the following compounds have been prepared.

*Metasaccharin phenylhydrazide*,  $C_{12}H_{18}O_5N_2$ , obtained by mixing the finely powdered lactone with three times its weight of 95% alcohol and rather less than its own weight of phenylhydrazine, crystallises from a mixture of methyl alcohol and ether in nodular aggregates, m. p.  $145^\circ$ .

*Parasaccharin phenylhydrazide* separates from water in an amorphous condition, which shows that it is not identical with Nef's parasaccharin, which gives a phenylhydrazide, m. p.  $125^\circ$ .

Metasaccharin when heated over a water-bath with water and brucine yields a salt,  $C_{29}H_{38}O_{10}N_2 \cdot 3H_2O$ , which separates from a mixture of aqueous alcohol and ether in colourless, glistening cubes or hexagonal plates, m. p.  $136^\circ$ ,  $[\alpha]_D -12^\circ$ .

Parasaccharin under similar conditions yields a brucine salt,  $C_{29}H_{38}O_{10}N_2 \cdot H_2O$ , which forms nodular aggregates, m. p.  $137^\circ$ , with loss of water; it has  $[\alpha]_D -27^\circ$ . The brucine salt of Nef's parasaccharin forms glistening needles, m. p.  $193-194^\circ$ .

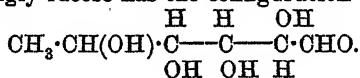
Although the melting points of the brucine salts of meta- and para-saccharin lie so close together, the two substances were proved to be different by showing that the melting point of a mixture of the two lay considerably below the melting point of either alone. P. H.

**Inversion of Sucrose by Invertase. III.** O. S. HUDSON (*J. Amer. Chem. Soc.*, 1909, 31, 655—664. Compare Abstr., 1908, i, 605, 856).—Since  $\alpha$ -dextrose, liberated from sucrose by invertase, changes to  $\beta$ -dextrose at  $30^\circ$  at a rate identical with that of the mutarotation of dextrose, it is to be expected that the freshly liberated laevulose will change similarly with a velocity equal to that of the mutarotation of laevulose. Since the latter proceeds rapidly at  $30^\circ$ , the experiments have been executed at  $0^\circ$ . In two experiments at  $0^\circ$ , with 1 litre of 5% sucrose and 100 c.c. of especially active invertase solution and with 1 litre of 8% sucrose and 500 c.c. of the invertase solution respectively, it is shown that the inversion of the sucrose proceeds almost instantaneously, the subsequent slow change of rotation with time being due to the change of the freshly liberated dextrose and laevulose to their stable states. The results are expressed graphically. The first rapid decrease of the rotation is due to the change of the freshly formed laevulose to its stable state, and the succeeding very slow change is due to the conversion of  $\alpha$ -dextrose into  $\beta$ -dextrose. By extrapolation, the value  $110^\circ$  at  $0^\circ$  is obtained for the specific rotatory power of  $\alpha$ -dextrose, which agrees with the value observed directly,  $109^\circ$  at  $20-30^\circ$ . From the values of the rotation in the first twenty-five minutes, the velocity coefficient of the change of the freshly formed laevulose into its stable form is calculated from the equation for a unimolecular reaction and its value is almost identical with that of the mutarotation of laevulose. The freshly formed laevulose is therefore the suspected, but hitherto unknown,  $\alpha$ -laevulose; its specific rotatory power, calculated from the data of the preceding experiments, is  $17^\circ$ .

The cause of the discrepancy between this and the value,  $-77^\circ$ , calculated by a different method (*loc. cit.*) is being investigated. The specific rotation of sucrose,  $66^\circ$ , is additively related to those of its component sugars,  $109^\circ$  for  $\alpha$ -dextrose and  $17^\circ$  for  $\alpha$ -lævulose. It is also shown that the rotation of raffinose,  $124^\circ$ , is equal to the sum of those of its constituents,  $\alpha$ -melibiose,  $171^\circ$ , and  $\alpha$ -lævulose,  $17^\circ$ . It appears to hold in general that the union of  $\alpha$ -dextrose and  $\alpha$ -lævulose carries with it an additive relation between the rotatory powers of the constituents and their compound. It is also a fact, and probably a closely related one, that  $\alpha$ -dextrose and  $\alpha$ -lævulose always combine to give a non-reducing, non-mutarotating sugar, such as sucrose, raffinose, or stachyose.

Experiments are described which indicate that brewers' yeast attacks  $\alpha$ -dextrose slightly more rapidly than  $\beta$ -dextrose. C. S.

**Fucose.** BERNHARD TOLLENS and F. RORIVE (*Ber.*, 1909, 42, 2009—2012; *Zeitsch. Ver. Deut. Zuckerind.*, 1909, 579—585).—Fifty grams of fucose were obtained from 6000 grams of dried *Fucus* from Heligoland. Fucose does not form a crystalline hydrate. It shows mutarotation having  $[\alpha]_D - 124.1^\circ$  ten minutes after solution, and a final value of  $-75.6^\circ$ . The initial value is calculated as  $-150^\circ$ . The final value for the rotation of the fucohexonic acid prepared by means of the addition of hydrogen cyanide, etc. (compare Mayer and Tollens, *Abstr.*, 1907, i, 588) is  $[\alpha]_D + 37.6^\circ$ . The oxidation of fucose (*loc. cit.*) and of rhamnose with dilute nitric acid has been carried out under identical conditions. The trihydroxyglutaric acid from fucose has  $[\alpha]_D + 27.6^\circ$ , and its potassium salt,  $[\alpha]_D - 8.2^\circ$  and  $-8.7^\circ$ ; that from rhamnose has  $[\alpha]_D - 24.9^\circ$ , and its potassium salt,  $+8.5^\circ$ . The acids are optical antipodes, accordingly fucose has the configuration:



E. F. A.

**Molecular and Solution Volumes of Colloidal Carbohydrates.** CHARLES F. CROSS and EDWARD J. BEVAN (*Ber.*, 1909, 42, 2198—2204).—The gram-molecular volume of solid anhydrous starch is 98.5, and the molecular solution volume for soluble starch is 92.6—93.3, whereas the value calculated from the formula  $\text{C}_6\text{H}_{10}\text{O}_5$ , using Traube's numbers, is 102.6. This difference is much greater than that observed by Traube in the case of various mono- and disaccharoses, but is comparable with the differences met with in the case of certain cyclic carbohydrates, for example, quercitol and inositol. The authors put forward the suggestion that ring formation may be the cause of the differences between the experimental and calculated values in the case of soluble starch.

In the case of the nitrate esters of cellulose it is found that the introduction of each  $\text{NO}_2$ -group has the same effect on the molecular volume, namely, an increment of 26.8 cm. In the case of the nitrates of other aliphatic alcohols, for example, glycerol, the effect of the nitro-groups on the molecular volume diminishes from the first to the third.

ISIDOR TRAUBE (*ibid.*, 2204), in a short, critical note, supports the authors' views.  
J. J. S.

**Soluble Starch.** CHARLES TANRET (*Compt. rend.*, 1909, 148, 1775—1776).—When soluble starch is prepared by Wolff's method (*Abstr.*, 1905, i, 510) a sparingly soluble product is also formed, having  $[\alpha]_D$  208—210°, and resembling the amylocellulose of Maquenne and Roux (*Abstr.*, 1905, i, 511). The soluble portion is not a single substance, since fractional precipitation of its aqueous solution by alcohol resolves it into two substances having  $[\alpha]_D$  180.5° and 173°, and giving with iodine reddish-violet and red colorations respectively. The alcoholic mother liquor contains a mixture of erythrodestrins having  $[\alpha]_D$  + 154.5°.

The author also describes substances obtained by varying the conditions under which starch is rendered soluble, and shows in each case that the product is not homogeneous.  
W. O. W.

**Organic Tungstates.** JOHN B. EKELEY (*J. Amer. Chem. Soc.*, 1909, 31, 664—666).—Freshly prepared tungstic acid dissolves in aqueous solutions of most aliphatic amines, forming substituted ammonium tungstates, which generally crystallise out on evaporation. When heated, the amine is driven off, and the tungstic acid is partially reduced to the blue oxide. The following are described: *Methylammonium tungstate*,  $(\text{NMe}_3)_6\text{W}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ ; *dimethylammonium tungstate*,  $(\text{NMe}_2\text{H})_{10}\text{W}_{12}\text{O}_{41} \cdot 13\text{H}_2\text{O}$ ; *trimethylammonium tungstate*,  $(\text{NMe}_3\text{H})_3\text{W}_4\text{O}_{13} \cdot \text{H}_2\text{O}$ ; *ethylammonium tungstate*,  $(\text{NEt}_3)_6\text{W}_7\text{O}_{24} \cdot 5\text{H}_2\text{O}$ ; *diethylammonium tungstate*,  $(\text{NEt}_2\text{H})_2\text{W}_4\text{O}_{13} \cdot 3\text{H}_2\text{O}$ ; *propylammonium tungstate*,  $(\text{NPr}_3\text{H})_{10}\text{W}_{12}\text{O}_{41} \cdot 6\text{H}_2\text{O}$ ; *dipropylammonium tungstate*,  $(\text{NPr}_2\text{H})_2\text{W}_4\text{O}_{13} \cdot \text{H}_2\text{O}$ ; *diamylammonium tungstate*,  $[\text{N}(\text{C}_5\text{H}_{11})_2\text{H}_2]_2\text{W}_5\text{O}_{16}$ ; and *ethylenediammonium tungstate*,  $\text{C}_2\text{H}_{10}\text{N}_2\text{W}_2\text{O}_7$ .  
C. S.

**Acid Haloid Salts.** II. FELIX KAUFER and E. KUNZ (*Ber.*, 1909, 42, 2482—2487. Compare this vol., i, 136).—Various bases have been examined with respect to the capacity of forming perhydrobromides and iodides. As a rule, the per-iodides are least, and the corresponding chlorides most, stable.

The following compounds are described: *Trimethylamine trihydrochloride*,  $\text{NMe}_3 \cdot 3\text{HCl}$ , pale yellow liquid, not solid at  $-28^\circ$ . *Tetraethylammonium chloride trihydrochloride*,  $\text{NEt}_4\text{Cl} \cdot 3\text{HCl}$ , solidifies at  $-6^\circ$  to  $-7^\circ$ . *Trimethylamine dihydrobromide*,  $\text{NMe}_3 \cdot 2\text{HBr}$ . *Tetramethylammonium bromide hydrobromide*,  $\text{NMe}_4\text{Br} \cdot \text{HBr}$ . *Tetraethylammonium bromide dihydrobromide*,  $\text{NEt}_4\text{Br} \cdot 2\text{HBr}$ . *Dimethylaniline dihydrobromide*,  $\text{NPhMe}_2 \cdot 2\text{HBr}$ , brown liquid. *Diethylaniline dihydrobromide*,  $\text{NPhEt}_2 \cdot 2\text{HBr}$ , colourless, hygroscopic crystals, m. p.  $37.3^\circ$ . *Dimethyl-o-toluidine dihydrobromide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NMe}_2 \cdot 2\text{HBr}$ , m. p.  $29.6^\circ$ . *Tetramethyldiaminodiphenylmethane trihydrobromide*,  
 $\text{CH}_3(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_3 \cdot 3\text{HBr}$ .

*Dimethylamine hydriodide*,  $\text{NHMe}_2 \cdot \text{HI}$ , m. p.  $147^\circ$ . *Tetraethylammonium iodide trihydriodide*,  $\text{NEt}_4\text{I} \cdot 3\text{HI}$ . *Quinoline dihydriodide*,  $\text{C}_8\text{H}_7\text{N} \cdot 2\text{HI}$ .

*Dimethylaniline dihydriodide*,  $\text{NPhMe}_2 \cdot 2\text{HI}$ , reddish-brown oil. The introduction of alkyl groups into the amine molecules tends to render the salts more stable. Negative radicles, on the other hand, tend to inhibit the formation of perhaloid salts.

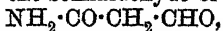
J. J. S.

**Behaviour of  $\alpha$ -Amino-acids towards Sodium Hypochlorite.** KURT LANGHELD (*Ber.*, 1909, 42, 2360—2374).—In cold aqueous solution, neutral sodium hypochlorite, free from chlorate, reacts with  $\alpha$ -amino-acids containing primary or secondary amino-groups to form the sodium salt of the chlorinated amino-acid. The solution of the sodium salt liberates iodine from potassium iodide, and by acidification with dilute acetic acid a solution of the chlorinated amino-acid is obtained; only in the cases of chloroleucine and dichloroleucine have the substances been isolated. The aqueous solutions of the sodium salts decompose in a simple way by heating, yielding sodium chloride, carbon dioxide, ammonia or an amine, and an aldehyde or ketone. The formation and decomposition of the salts can be represented thus:

$$\text{NHR} \cdot \text{CR}'\text{R}'' \cdot \text{CO}_2\text{H} \xrightarrow{\text{NaOCl}} \text{NRCl} \cdot \text{CR}'\text{R}'' \cdot \text{CO}_2\text{Na} \rightarrow \text{NaCl} + \text{CO}_2 + \text{NR} \cdot \text{CR}'\text{R}'' \xrightarrow{\text{H}_2\text{O}} \text{NH}_2\text{R} + \text{R}'\text{COR}''.$$

In order that the decomposition may occur without complications, it is necessary that the hypochlorite, the amino-acid, and the products of decomposition should be in contact for as brief a period as possible; an apparatus is described which satisfies this condition. Since substituted acid amides, amino-acids containing a tertiary amino-group, and certain proteins, such as egg-albumin, gelatin, and casein, do not react, or only slightly, with sodium hypochlorite, the reaction may serve to separate polypeptides which do not contain the group  $\text{C}(\text{NH}_2) \cdot \text{CO}_2\text{H}$  from amino-acids and peptones with this reactive complex.

The following substances have been decomposed by sodium hypochlorite: glycine, sarcosine, alanine,  $\alpha$ -aminoisobutyric acid, *i*-valine, *i*-leucine, phenylalanine, aspartic acid, asparagine, glutamic acid, tyrosine, serine, *i*-proline, and histidine, and the following new compounds have been obtained:  $\beta$ -iminazoleacetaldehyde from histidine, isolated as the *hydrochloride*,  $\text{C}_5\text{H}_5\text{ON}_2 \cdot \text{HCl}$ ; a *pyrroline* from proline, isolated as the *hydrochloride*,  $\text{C}_4\text{H}_8\text{N} \cdot \text{HCl}$ ; *p*-hydroxyphenylacetaldehyde from tyrosine, isolated as the *p*-nitrophenylhydrazone,  $\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}_3$ , which separates from alcohol in crystals containing 1 mol.  $\text{EtOH}$ , m. p.  $158^\circ$ ; the amide of the semialdehyde of malonic acid,



from asparagine, isolated as the *phenylhydrazone*,  $\text{C}_9\text{H}_{11}\text{ON}_3$ , m. p.  $239\text{--}240^\circ$ .

C. S.

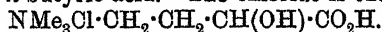
**Constituents of Meat Extract.** R. ENGELAND (*Ber.*, 1909, 42, 2457—2462. Compare this vol., ii, 71).—Carnitine (*Abstr.*, 1905, i, 726; 1907, i, 264; 1908, i, 41, 842) contains a carboxylic group as the hydrochloride, and when heated with an ethyl alcoholic solution of hydrogen chloride yields the *ester*, which can be isolated as the *platinichloride*. This salt, unlike the platinichloride of carnitine, is sparingly soluble in water. The ester, when treated with gold chloride solution, is hydrolysed, and yields carnitine aurichloride.

Novaine (Abstr., 1907, i, 18, 114) behaves in exactly the same manner as carnitine, and is probably identical with it. Novaine contains an impurity, probably homobetaine, which remains in the mother liquor when carnitine ester platinichloride crystallises from the solution obtained by esterifying novaine and subsequently treating with platinic chloride. The compound described by Krimberg as oblitine (Abstr., 1908, i, 842) is in all probability carnitine ethyl ester.

Carnitine also contains an alcoholic hydroxyl group, as the dry chloride of the ester reacts with acetyl chloride, yielding a *monoacetyl* derivative of carnitine,  $\text{OAc} \cdot \text{C}_6\text{H}_4\text{NCl} \cdot \text{CO}_2\text{H}$ , the *platinichloride* of which,  $(\text{C}_8\text{H}_{14}\text{O}_4\text{N})_2\text{PtCl}_6$ , forms pale yellow crystals, m. p.  $199^\circ$ .

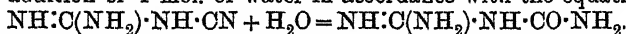
When an aqueous solution of carnitine chloride is made alkaline with sodium carbonate and oxidised with calcium permanganate,  $\beta$ -homobetaine is obtained. The ethyl ester of homobetaine forms a *platinichloride*,  $2\text{C}_8\text{H}_{18}\text{O}_2\text{N} \cdot \text{PtCl}_6$ , which crystallises from water in orange-red needles, m. p.  $210$ — $211^\circ$  (decomp.).

These reactions point to the conclusion that carnitine is an  $\alpha$ -hydroxy- $\gamma$ -trimethylamino-*n*-butyric acid. The chloride is therefore



J. J. S.

**The Chemical Nature of Dicyanodiamide.** N. CARO and HERMANN GROSSMANN (*Chem. Zeit.*, 1909, 33, 734. Compare *ibid.*, 1907, 31, 1195, and *Zeitsch. angew. Chem.*, 1909, 22, 1182).—Radlberger having described salts of dicyanodiamide with certain acid dyes (Abstr., 1908, i, 1001), the neutral character of this substance required further establishment. It is found, on careful repetition of Radlberger's work that salts of dicyanodiamide do not exist, those described by him being salts of dicyanodiamidine, which is produced from dicyanodiamide by the addition of 1 mol. of water in accordance with the equation:



Most probably some quantity of this substance accompanied the dicyanodiamide used by Radlberger.

Conductivity measurements, the activity towards various indicators (Abstr., 1907, ii, 389), and the effect on the optical rotation of tartaric acid solutions (*Chem. Zeit.*, 1907, 31, 1195), all give additional evidence of the neutrality of dicyanodiamide.

J. V. E.

**Hexathiocyno-salts of Molybdenum.** ARTHUR ROSENHEIM (*Ber.*, 1909, 42, 2295—2296).—Crystallographic measurements have been made of the series of salts  $\text{M}_3\text{X}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$ , in which  $\text{M} = \text{K}, \text{NH}_4$ , or  $\text{Na}$ , and  $\text{X} = \text{Mo}$  or  $\text{Cr}$ . It is found that the molybdenum or chromium salts are not isomorphous amongst themselves, but that each molybdenum salt is isomorphous with the corresponding chromium salt, the potassium salts being pseudo-hexagonal, the ammonium salts rhombic, and the sodium salts asymmetric.

The results support the view that the potassium molybdenum salt is  $\text{K}_3[\text{Mo}(\text{SCN})_6] \cdot 4\text{H}_2\text{O}$ , and not, as supposed by Maas and Sand (Abstr., 1908, i, 961),  $\text{K}_3[\text{Mo}(\text{SCN})_6\text{H}_2\text{O}] \cdot 4\text{H}_2\text{O}$ .

C. H. D.

Nitroacetonitrile. V. Nitroacetic Acid. WILHELM STEINKOPF (*Ber.*, 1909, 42, 2026—2031. Compare this vol., i, 216).—Adopting the constitution of fulminic acid as nitrocyanoacetamide, it appeared possible to hydrolyse the amide group to nitrocyanoacetic acid. When concentrated potassium hydroxide is used to effect hydrolysis, the reaction goes further, the cyano-group being also hydrolysed, so that potassium nitromalonate,  $\text{OK} \cdot \text{NO} : \text{C}(\text{CO}_2\text{K})_2$ , is first formed, and, losing potassium carbonate, is converted into potassium nitroacetate,  $\text{OK} \cdot \text{NO} : \text{CH} \cdot \text{CO}_2\text{K}$ . This crystallises well, gives an intense red coloration with ferric chloride, and forms a colourless salt with lead acetate, and yellow salts with mercuric chloride or silver nitrate. These all explode in the flame. Potassium nitroacetate was obtained from ammonium fulminate, from nitroacetonitrile, from nitroacetamide, and from methazonic acid—the last substance giving a pure product in good quantity. This behaviour affords proof of the presence of the  $-\text{C}-\text{C}-$  group in methazonic acid. E. F. A.

Application of the Theory of Complex Ions to the Reactions of Mercury Cyanide with Silver Salts and Alkali Hydroxides. KARL A. HOFMANN and H. WAGNER (*Zeitsch. Elektrochem.*, 1909, 15, 441—447).—Mercuric cyanide combines with anions to complex anions of the form  $\text{Hg}(\text{CN})_2\text{X}'$ . By measuring the solubility of mercury cyanide in different salts, the values of  $k = [\text{Hg}(\text{CN})_2\text{X}'] / [\text{Hg}(\text{CN})_2][\text{X}']$  are found to be for  $\text{NO}_3'$ , 0.43; for  $\text{OH}'$ , 1.68, and for  $\text{CN}'$ , about 40. It appears that the greater the tendency of a group of atoms to assume an electric charge, the less tendency it has to combine with mercury cyanide. The complex ions split up also, thus:  $\text{Hg}(\text{CN})_2\text{X}' \rightleftharpoons \text{Hg}(\text{CN})\text{X} + \text{CN}'$ , and this decomposition proceeds much further when X is a weak ion, such as  $\text{CH}_3 \cdot \text{COO}'$ , than in the case of a strong one, like  $\text{NO}_3'$ . For this reason, a precipitate of silver cyanide is formed when mercuric cyanide is treated with silver acetate or nitrite, but not when silver nitrate is used. T. E.

Results of Cooling certain Hydrated Platinocyanides in Liquid Air. J. EMERSON REYNOLDS (*Proc. Roy. Soc.*, 1909, 82, A, 380—383).—It was observed that when a specimen labelled lithium platinocyanide was cooled in liquid air, the original white compound became red and regained its original colour on warming, but after repeated cooling and warming, it assumed a yellow colour in liquid air, which was retained at the ordinary temperature. It was found that the salt was a very impure lithium platinocyanide,  $\text{Li}_2\text{Pt}(\text{CN})_6$ , and the explanation of this behaviour has been found in the properties of this salt, which is white when anhydrous, whilst the monohydrate is yellow, the dihydrate orange-red, and the trihydrate colourless.

The trihydrate is obtained in needles by evaporating the aqueous solution at 40—50° and suddenly cooling to 15°; on heating cautiously, or on cooling in liquid air, it gives the red dihydrate. The monohydrate is best obtained by evaporating a solution of the trihydrate to which a hydrated salt, for example, sodium sulphate, has been added, and then cautiously heating the residue, or by repeated cooling in liquid air of the trihydrate, mixed with a salt having affinity for water.

Lithium platinocyanide,  $\text{Li}_2\text{Pt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ , grass-green crystals, is scarcely affected by cooling in liquid air. G. S.

**Hydrazo- and Azo-methane.** JOHANNES THIELE (*Ber.*, 1909, 42, 2575—2580).—*s*-Diformyldimethylhydrazine,  $\text{CHO} \cdot \text{NMe} \cdot \text{NMe} \cdot \text{CHO}$ , prepared from diformylhydrazine and methyl sulphate in alkaline solution, extraction with ether, and crystallisation of the oil by addition of a little ethyl acetate, forms glistening crystals, m. p.  $52^\circ$ .

By acidifying the alkaline solution without isolating the dimethyl derivative, evaporating, distilling with sodium hydroxide, and absorbing the distillate in hydrochloric acid, *s*-dimethylhydrazine dihydrochloride is obtained. It does not yield yellow products with aldehydes. When a concentrated solution of the hydrochloride is dropped into potassium chromate, azomethane is formed, and is pumped off and condensed by means of carbon dioxide and ether.

*Azomethane*,  $\text{CH}_3 \cdot \text{N} \cdot \text{N} \cdot \text{CH}_3$ , is a colourless gas, b. p.  $1.8^\circ/756$  mm. (corr.),  $D_{15}^0$  0.744, vapour density 32. For analysis, it is largely diluted with carbon dioxide or nitrogen, and passed into the combustion tube. It is very soluble in water to a neutral solution. The liquefied compound is faintly yellow; it solidifies not far below  $-78^\circ$  to colourless leaflets. It explodes on heating or sparking, forming nitrogen, methane, ethylene, hydrogen, and a little ethane. If diluted with inert gas and heated, it forms ethane and nitrogen.

Acids decompose its solution into formaldehyde and methylhydrazine. Zinc dust and sodium hydroxide reduce it to *s*-dimethylhydrazine.

C. H. D.

**Action of Cacodylic and Methylarsinic Acids on Antimony Trichloride.** LÉONCE BARTHE and ADOLPHE MINET (*Compt. rend.*, 1909, 148, 1609—1611).—A syrupy solution of cacodylic acid reacts with deliquescent antimony trichloride, forming *dichloroantimony cacodylate*,  $\text{O} \cdot \text{AsMe}_2(\text{OSbCl}_2)$ . This is a stable compound, crystallising in long, lustrous, acicular prisms, sparingly soluble in hot water and alcohol.

When a solution of methylarsinic acid is saturated with sodium hydrogen carbonate, heated to boiling, and treated with antimony trichloride, a precipitate appears which becomes crystalline on digestion. This consists of *antimonyl methylarsinate*,  $\text{MeAsO}(\text{OSbO})_2$ .

Details are given of a method for the analysis of compounds of this type. W. O. W.

**Molecular Rearrangements in the Camphor Series. II. Laurolene.** WILLIAM A. NOYES and C. G. DERICK (*J. Amer. Chem. Soc.*, 1909, 31, 669—673. Compare this vol., i, 133).—Laurolene, obtained from aminolauronic acid hydrochloride and sodium nitrite (Tiemann, *Abstr.*, 1901, i, 5), and having  $[\alpha]_D^{25}$   $22.8^\circ$  and  $D_{15}^{25}$  0.8030, yields by oxidation with cold dilute alkaline potassium permanganate a product which appears to be a diketone that has partly condensed to an unsaturated cyclic monoketone. Since the pure ketone could not be obtained, the experiment has been repeated on laurolene obtained

by boiling the nitroso-compound of aminolauroic anhydride with 10% sodium hydroxide, and having  $[\alpha]_D^{20} - 14.5^\circ$  and  $D_{15}^{25} 0.8043$ . The hydrocarbon is oxidised at  $0^\circ$  by 2% potassium permanganate. The oxidation product and unchanged laurolene are extracted by ether and separated by distillation under diminished pressure. The oxidation product distils as an oil, but the last portions solidify to a substance, m. p.  $68^\circ$  (corr.), of the same composition,  $C_{15}H_{14}O_2$ , as the oil. The substance has  $D_{15}^{25} 0.9888$  and  $[\alpha]_D^{25} - 8.5^\circ$  in 32.5% ethereal solution, and forms an oily oxime and hydrazone and an impure semicarbazone. Its constitution is briefly discussed, and the deduction drawn that Eykman's formula (Abstr., 1907, i, 378) most probably represents correctly the constitution of laurolene. C. S.

**A Peculiar Method of Formation of Nitrobenzene from *m*-Dinitrobenzene.** MORITZ KOHN (*Monatsh.*, 1909, 30, 397—399. Compare Schultze, Abstr., 1897, i, 40; Meisenheimer and Patzig, Abstr., 1906, i, 642, 652).—Nitrobenzene is formed by boiling *m*-dinitrobenzene with an aqueous alkaline solution of hydroxylamine for about thirty minutes. W. H. G.

**The Preparation of Benzenesulphonyl Chloride.** RUDOLF PUMMERER (*Ber.*, 1909, 42, 2274—2275. Compare this vol., i, 465; Ullmann and Korselt, Abstr., 1907, i, 306).—In the action of chlorosulphonic acid on benzene, a temperature of  $25^\circ$  gives a better yield of benzenesulphonyl chloride than one of  $5^\circ$ . C. H. D.

**Action of Nitric Acid on Triphenylmethane.** ROBERT SCHWARZ (*J. Amer. Chem. Soc.*, 1909, 31, 848—850).—It has been shown by E. and O. Fischer (Abstr., 1879, 384) that trinitrotriphenylmethane can be prepared readily by the action of nitric acid ( $D 1.5$ ) on triphenylmethane. Smith (Abstr., 1897, i, 573), in attempting to prepare this nitro-compound, obtained triphenylcarbinol, but on repeating the experiment was unable to get the same result.

Experiments have now been carried out in order to ascertain the conditions under which the carbinol and trinitro-compound respectively are produced. It has been found that, under varying conditions, the action of nitric acid on triphenylmethane results in the formation of trinitrotriphenylmethane, triphenylcarbinol, and a red oil of unknown composition. When the hydrocarbon is added to strong fuming nitric acid at  $0^\circ$ , trinitrotriphenylmethane is produced. If small quantities of red, fuming acid of about  $D 1.48$  are added to triphenylmethane and the reaction takes place at a moderate temperature, triphenylcarbinol is obtained, but trinitrotriphenylmethane is not produced. If, however, stronger acid is used under the latter conditions and the temperature is allowed to rise to the boiling point, the red oil is formed. The best yield of triphenylcarbinol obtained amounted to about 45% of the theoretical. E. G.

**The Dinaphthylmethane Series.** JULIUS SCHMIDLIN and PAUL MASSINI (*Ber.*, 1909, 42, 2377—2392).—The paper describes deriv-  
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atives of *aa*-dinaphthylmethane; attempts to prepare from them the parent hydrocarbon have been unsuccessful.

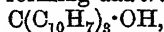
*aa*-*Dinaphthylcarbinol*,  $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{OH}$ , m. p. 146—147° (corr.), obtained from magnesium  $\alpha$ -naphthyl bromide and ethyl formate in ethereal solution, forms colourless needles, develops a greenish-blue coloration with sulphuric acid, and is readily converted by alcohol and hydrochloric acid into the *ethyl ether*,  $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{OEt}$ , m. p. 136° (corr.). *aa*-*Dinaphthylmethyl chloride*,  $\text{CH}(\text{C}_{10}\text{H}_7)_2\text{Cl}$ , m. p. 188—189° (corr.), obtained from hydrogen chloride and the carbinol in benzene solution, forms colourless needles, develops a faint green coloration with sulphuric acid, and is reconverted into the carbinol by boiling water. By shaking its benzene solution with dry "molecular" silver, *tetranaphthylethane*,  $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{CH}(\text{C}_{10}\text{H}_7)_2$ , m. p. 285—286° (corr.), is obtained, which is also produced by the action of magnesium phenyl iodide or magnesium naphthyl bromide on dinaphthylmethyl chloride. The reaction between carbon dioxide and ethereal magnesium *aa*-dinaphthylmethyl chloride leads to the formation of *aa*-*dinaphthyl acetic acid*,  $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{CO}_2\text{H}$ , m. p. 228.5° (corr.), which forms a *silver salt*, m. p. 205° (decomp.), *copper salt*, m. p. 205° (decomp.), and, by heating with phosphoric chloride and acetyl chloride, a *chloride*,  $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{COCl}$ , which loses carbon monoxide at its m. p., 167—169° (corr.), and does not readily lose its halogen by treatment with water, alkalis, or silver.

*aa*-*Dinaphthylfluorene*,  $\text{CH}_2\text{C}(\text{C}_{10}\text{H}_6)_2$ , m. p. 242.5° (corr.), is obtained when *aa*-dinaphthylcarbinol is heated with zinc, glacial acetic acid, and a little concentrated hydrochloric acid; it forms a strongly violet-red fluorescent solution in benzene. Cold fuming nitric acid converts *aa*-dinaphthylcarbinol into a *tetranitro*-derivative, m. p. 190—193° (decomp., corr.). *aa*-*Dinaphthyl ketone*,  $\text{CO}(\text{C}_{10}\text{H}_7)_2$ , m. p. 104° (corr.), is the final product of the reaction between magnesium  $\alpha$ -naphthyl bromide and naphthoyl chloride in ethereal solution.  *$\alpha$ -Naphthylmethyl bromide*,  $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\text{Br}$ , b. p. 183°/18 mm., obtained from  $\alpha$ -methylnaphthalene and bromine at 200°, does not react with ethereal magnesium  $\alpha$ -naphthyl bromide, but by distillation the mixture yields *aa*-dinaphthyl.

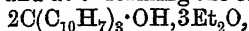
In boiling glacial acetic acid *aa*-dinaphthylcarbinol condenses with phenol to form the *ether*,  $\text{CH}(\text{C}_{10}\text{H}_7)_2\cdot\text{OPh}$ , m. p. 217—219° (corr.); with  $\alpha$ -naphthol, with aniline hydrochloride, and with  $\alpha$ -naphthylamine to form *substances* of undetermined constitution, m. p. 278.5—279.5°, 233—238°, and 215° (all corr.) respectively. C. S.

*$\alpha$ -Dinaphthyl Ketone*. HUGO BAUER (*Ber.*, 1909, 42, 2588—2589). —By oxidising  *$\alpha$ -dinaphthylcarbinol* with chromic acid, the author in conjunction with Reichardt some years ago prepared the  *$\alpha$ -dinaphthyl ketone* recently described by Schmidlin and Massini (preceding abstract); at the same time phenyl- $\beta$ -methoxynaphthylcarbinol, colourless needles, m. p. 237°, was prepared by the interaction of benzaldehyde and the magnesium compound of  $\alpha$ -iodo- $\beta$ -methoxynaphthalene; *phenylbenzyl- $\alpha$ -naphthylcarbinol*, colourless crystals, m. p. 149—150°, was similarly obtained by acting on benzyl magnesium chloride with phenyl  $\alpha$ -naphthyl ketone. P. H.

The Trinaphthylmethane Series. JULIUS SCHMIDLIN and PAUL MASSINI (*Ber.*, 1909, 42, 2392—2404).—The interaction of  $\alpha$ -naphthoyl chloride and an excess of magnesium  $\alpha$ -naphthyl bromide in ether yields a compound,  $2C(C_{10}H_7)_3 \cdot OMgBr, 3Et_2O$ , which is decomposed by water, at the b. p. of ether forming *aaa-trinaphthylcarbinol*,



m. p. 168—169° (corr.), and at 0° forming the compound,



m. p. 103—104° (decomp., corr.). The latter loses its ether exceedingly slowly even in a vacuum, and by crystallisation from cold benzene is changed into the compound,  $3C(C_{10}H_7)_3 \cdot OH, C_6H_6$ , m. p. 123° (decomp., corr.). At 160° both substances lose ether or benzene, and are changed into a substance which in its properties is identical with *aaa-trinaphthylcarbinol*, although its m. p. cannot be raised above 131° by repeated crystallisation. Tri- $\alpha$ -naphthylcarbinol does not retain, when once formed, the property of uniting with ether or benzene, develops an orange-red colour with sulphuric acid, forms a yellow *hexanitro*-compound,  $C[C_{10}H_5(NO_2)_2]_3 \cdot OH$ , m. p. 236—241° (decomp., corr.), by nitration with fuming nitric acid, and contains a very immobile hydroxyl group. Mild reducing agents, thionyl chloride, or a molecular quantity of phosphorus pentachloride have no action. Hydriodic acid and amorphous phosphorus at 95° convert the carbinol into a *dihydro-aaa-trinaphthylcarbinol*,  $C_{31}H_{23} \cdot OH$ , m. p. 160—161° (corr.), whilst an excess of phosphorus pentachloride in acetyl chloride produces a *dichloro*-additive compound,  $C_{31}H_{21}Cl_2 \cdot OH$ , m. p. 238—239° (decomp., corr.). The carbinol, however, when heated in acetyl chloride with moist phosphoryl chloride, yields

*naphthylidinaphthylene* methyl chloride,  $C_{10}H_7 \cdot CCl \begin{smallmatrix} \nearrow C_{10}H_6 \\ \searrow C_{10}H_6 \end{smallmatrix}$ , m. p. 233—234°

(decomp., corr.), which crystallises in citron-yellow leaflets, develops an intense blue coloration with sulphuric acid, and is converted by "molecular" silver into *dinaphthylididnapthylene-ethane* (annexed formula), m. p. 180° (decomp.), a dark green, crystalline powder, which is stable in the air and gives a carmine-red colour with sulphuric acid.

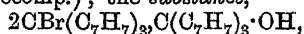
*aa $\beta$ -Trinaphthylcarbinol*,  $C(C_{10}H_7)_3 \cdot OH$ , m. p. 263—264° (corr.), obtained from  $\beta$ -naphthoyl chloride, forms colourless needles, and gives an orange-yellow colour with sulphuric acid. C. S.

2-Methylantracene from Ditolylmethane or Ditolyethane. OTTO FISCHER (*J. pr. Chem.*, 1909, ii, 79, 555—562).—Pure 2-methylantracene is obtained from ditolyethane, that from ditolylmethane being mixed with anthracene (*Abstr.*, 1875, 151). Bromine in carbon disulphide forms 9:10-*dibromo-2-methylantracene*, m. p. 142—143°, the positions of the halogen atoms being determined by the oxidation of the substance to 2-methylantraquinone. The latter and bromine at 130—140° yield a colourless *dibromomethylantraquinone*, m. p. 219—220°. C. S.

Hexabenzylethane and Its Derivatives. FRITZ SCHMERDA (*Monatsh.*, 1909, 30, 387—395).—The object of this investigation was to prepare tribenzylmethane from tribenzylcarbinol, and to pass from

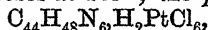
this to the homologue of rosaniline,  $\text{CH}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_3$ , but the only substance obtained by the reduction of the carbinol was hexabenzylethane.

*Tribenzylmethyl bromide*,  $\text{CBr}(\text{C}_7\text{H}_7)_3$ , prepared by the action of phosphorus pentabromide on tribenzylcarbinol, is a white, crystalline powder, m. p.  $157^\circ$  (decomp.); the substance,



has m. p.  $145^\circ$ . The *chloride*,  $\text{CCl}(\text{C}_7\text{H}_7)_3$ , formed by the action of an alcoholic solution of hydrogen chloride on the carbinol, crystallises in needles, m. p.  $145^\circ$  (decomp.).

*Hexabenzylethane*,  $\text{C}_2(\text{C}_7\text{H}_7)_6$ , is formed together with dibenzyl by heating tribenzylcarbinol with hydriodic acid under pressure at  $200^\circ$ ; it crystallises in large, transparent prisms, m. p.  $81^\circ$ , b. p.  $353\text{--}358/746$  mm.; the *hexanitro-derivative*,  $\text{C}_{44}\text{H}_{36}\text{O}_{12}\text{N}_6$ , is a yellow substance, which softens at  $75^\circ$  and decomposes at about  $115^\circ$ ; the *hexa-amino-derivative*,  $\text{C}_{44}\text{H}_{48}\text{N}_6$ , is a pale, yellowish-red powder, which sinters at  $61^\circ$  and decomposes at  $105^\circ$ ; the *platinichloride*,



is a somewhat unstable, yellow, crystalline substance. W. H. G.

**Electrochemical Reduction of *p*-Nitroacetanilide.** KURT BRAND and EDUARD STOHR (*Ber.*, 1909, 42, 2478—2482. Compare Abstr., 1907, i, 100, 206).—When *p*-nitroacetanilide is subjected to electrolytic reduction, using a solution of the anilide and sodium acetate in a mixture of alcohol, glacial acetic acid, and ethyl acetate as the cathode liquid, the chief product is *p*-hydroxylaminoacetanilide. This could not be isolated as such, but was oxidised to *p*-nitrosoacetanilide (Cain, *Trans.*, 1908, 93, 681), and was also obtained as

*benzylidene-p-hydroxylaminoacetanilide*,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{CHPh} \end{array}$ , which crystallises from alcohol in pale yellow plates, m. p.  $215^\circ$ . When hydrolysed with alcoholic potassium hydroxide or hydrogen chloride, the benzylidene derivative yields azoaniline and *p*-phenylenediamine.

When further reduced in acetic acid solution, the chief product is *p*-aminoacetanilide, the *benzylidene* derivative of which,  $\text{C}_{15}\text{H}_{14}\text{ON}_2$ , has m. p.  $165\text{--}166^\circ$ . When the nitro-compound is reduced in acid solution, the chief product is *p*-phenylenediamine. J. J. S.

**Coloured Isomeric Picrylamines.** MAX BUSCH and ERNST PUNGS (*J. pr. Chem.*, 1909, ii, 79, 546—554).—When alcoholic solutions of picryl chloride and the following amines are mixed, the picrylamine,  $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{NHR}$ , is deposited frequently in two differently coloured forms. *p*-Toluidine gives a mixture of labile, yellow prisms, m. p.  $163^\circ$ , and stable, blood-red needles, m. p.  $165^\circ$ ; the former alone are obtained by treating the alkaline alcoholic solution of the mixture with hydrochloric acid, whilst the red form separates when the mixture is crystallised from alcohol and benzene. *m*-Toluidine gives a mixture of yellow prisms, m. p.  $130^\circ$ , and orange-red needles, m. p.  $129\text{--}5^\circ$ . *p*-Xylidine gives only blood-red needles, m. p.  $163^\circ$ , but the labile, yellow form is obtained by acidifying the cold alkaline alcoholic solution. 1:3:4-Xylidine gives orange-red, monoclinic needles, m. p.

158°, which change at 190° to the orange-brown, triclinic needles, m. p. 159°. 1:3:2-Xylidine yields only citron-yellow leaflets, m. p. 212°.  $\psi$ -Cumidine gives a product which separates from acetone in blood-red, dichroic needles, m. p. 160°, and from alcohol containing hydrochloric acid in dichroic needles, m. p. 160°, of a lighter colour. *o*- and *p*-Anisidines form only orange-red, rhombic needles, m. p. 142° and 138° respectively, whilst *o*- and *p*-phenetidines give scarlet needles, m. p. 136—137°, and red needles, m. p. 123—124°, respectively. Methylaniline gives Turpin's reddish-brown leaflets, m. p. 108°, which, by slow heating, change to Sudborough and Picton's garnet-red prisms, m. p. 128—129°. C. S.

**Fission of Quaternary Ammonium Salts by Nascent Hydrogen.** HERMANN EMDE (*Ber.*, 1909, 42, 2590—2594).—The observation recorded previously (Abstr., 1906, i, 945) that cinnamyltrimethylammonium chloride is resolved by sodium amalgam into phenylpropylene and trimethylamine, whereas the corresponding chlorohydrin is not affected by this reagent, has led the author to study the action of nascent hydrogen on a number of quaternary ammonium salts with the object of determining what influence the olefinic grouping has on the stability of the carbon nitrogen linking in such compounds, but the investigation is not as yet sufficiently advanced to admit of any generalisations. The decomposition of dibenzyltrimethylammonium chloride and of phenylcinnamyltrimethylammonium chloride can be employed for the preparation of benzyltrimethylamine and of phenylpropylene.

Benzyltrimethylamine is obtained in 80% yield by heating together benzyl chloride and dimethylamine and treating the resulting product with water and an excess of 5% sodium amalgam; after the reaction, the oily layer, consisting of toluene and benzyltrimethylamine, is separated, washed, dried, and distilled.

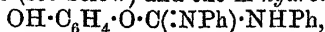
Phenylpropylene is obtained in almost theoretical yield by the action of sodium amalgam on phenylcinnamyltrimethylammonium chloride prepared by condensing cinnamyl chloride with dimethylaniline; the *platinchloride* of this quaternary salt,  $C_{34}H_{40}N_2Cl_6Pt$ , melts at 177°; a double salt with *cadmium chloride*,  $C_{34}H_{40}N_2Cl_4Cd$ , melts at 141°.

P. H.

**Carbodi-imides.** MAX BUSCH, GUSTAV BLUME, and ERNST PUNGS [and, in part, MARTIN FLEISCHMANN] (*J. pr. Chem.*, 1909, ii, 79, 513—546).—The paper deals with the additive compounds obtained from carbodiphenylimide and aromatic phenols or aminocarboxylic acids.

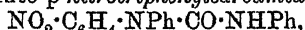
When carbodiphenylimide is heated at 150—160° with an equal molecular quantity of phenol, *p*-cresol, or  $\alpha$ - or  $\beta$ -naphthol, an *O*-ether of diphenyl- $\psi$ -carbamide,  $NPh_2C(OR)NHPh$ , is obtained. The *phenyl ether*,  $NPh_2C(OPh)NHPh$ , m. p. 104°, possesses basic properties [*oxalate*, m. p. 149° (decomp.); *picrate*, m. p. 204°], and is decomposed by warm dilute acids or alkalis, yielding phenol and diphenylcarbamide. The *p*-tolyl ether,  $NPh_2C(O\cdot C_6H_7)NHPh$ , has m. p. 111°, and the  $\alpha$ - and  $\beta$ -naphthyl ethers,  $NPh_2C(O\cdot C_{10}H_7)NHPh$ , have m. p. 205° and

201° respectively. Resorcinol and carbodiphenylimide at 120° form  $\gamma$ -carbodiphenylimide (see below) and the *m*-hydroxyphenyl ether,

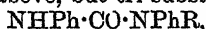


m. p. 147°. Phenyl mercaptan and carbodiphenylimide form in boiling benzene the *thiophenyl ether*,  $\text{NPh}\cdot\text{C}(\text{SPh})\cdot\text{NPh}$ , m. p. 82°, which is decomposed by acids into carbanilide and phenyl mercaptan.

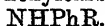
The mononitrophenols react with carbodiphenylimide only with difficulty. *p*-Nitrophenol in boiling benzene forms a substance, m. p. 100°, which is probably the *O*-ether,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}(\text{NPh})\cdot\text{NPh}$ , and changes at 160° into *p*-nitrotriphenylcarbamide,



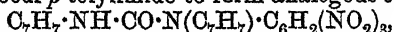
m. p. 152°, which is obtained directly when carbodiphenylimide and *p*-nitrophenol are heated at 140°, and also from *p*-nitrodiphenylamine and phenylcarbimide on the water-bath. 2:4-Dinitrophenol and picric acid react easily with carbodiphenylimide in boiling benzene, yielding, not *O*-ethers as above, but tri-substituted carbamides,



the evidence for this constitution being the lack of basic properties and the ready decomposition into phenylcarbimide and diarylamine,



2:4-Dinitrotriphenylcarbamide,  $\text{NHPH}\cdot\text{CO}\cdot\text{NPh}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ , forms yellow needles, and decomposes into phenylcarbimide and 2:4-dinitrodiphenylamine at its m. p., 134—135°, whilst 2:4:6-trinitrotriphenylcarbamide,  $\text{NHPH}\cdot\text{CO}\cdot\text{NPh}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ , m. p. 213—214°, decomposes in a similar manner. Picric acid unites with carbodi-*o*-tolylimide or carbodi-*p*-tolylimide to form analogous compounds,



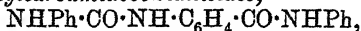
m. p. 210° and 210—211° respectively, which decompose in a similar manner.

The action of di- and tri-nitrophenols on carbodiphenylimide serves to explain the behaviour of the latter with carboxylic acids. Dains claims (Abstr., 1899, i, 592) that acetic acid and carbodiphenylimide yield acetic anhydride and carbanilide. Acetanilide and carbon dioxide are also produced, however, and the formation of the four substances is indicated in the reactions: (I)  $\text{C}(\text{NPh})_2 + \text{Ac}\cdot\text{OH} = \text{NHPH}\cdot\text{CO}\cdot\text{NPhAc} \rightarrow \text{NPhCO} + \text{PhNHAc}$ ; (II)  $2\text{NPhCO} + 2\text{Ac}\cdot\text{OH} = \text{CO}(\text{NHPH})_2 + \text{Ac}_2\text{O} + \text{CO}_2$ . These reactions have been verified experimentally, and the acetyldiphenylcarbamide has been isolated by the interaction of acetic acid and carbodiphenylimide in petroleum ether. Since it readily decomposes into phenylcarbimide and acetanilide, its formation at 150° by Creath (Abstr., 1875, 885) and Kühn (Abstr., 1885, 260) is doubtful, but it can be obtained in 15% yield from phenylcarbimide and acetanilide on the water-bath.

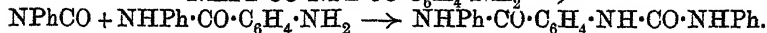
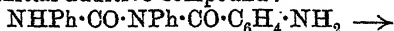
Equal molecular quantities of carbodiphenylimide and *o*-aminophenol in boiling benzene react to form an additive compound, the point of attack being the nitrogen and not the oxygen atom; in consequence of its amphoteric character and the absence of an amino-group, the compound is regarded as *o*-hydroxytriphenylguanidine,  $\text{NHPH}\cdot\text{C}(\text{NPh})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , m. p. 132—133°. In a similar way carbodiphenylimide and phenylhydroxylamine yield *triphenylhydroxy-*

guanidine,  $\text{NPh}\cdot\text{C}(\text{NPh})\cdot\text{NPh}\cdot\text{OH}$ , m. p.  $154^\circ$ , which forms triphenylguanidine by reduction.

Carbodiphenylimide attacks aminocarboxylic acids at the carboxyl group. With *m*- and *p*-aminobenzoic acids in boiling benzene the corresponding *phenylcarbamidobenzanilides*,



m. p.  $250$ — $254^\circ$  and  $>300^\circ$  respectively, are formed by the decomposition of the initial additive compound:



In the case of anthranilic acid, the *o*-phenylcarbamidobenzanilide suffers ring closure with loss of aniline, phenyldiketotetrahydroquinazoline being produced.

When carbodiphenylimide is heated with different phenols, a crystalline by-product is obtained in larger or smaller quantity; it is best obtained by saturating a cold benzene solution of phenol and  $\alpha$ -carbodiphenylimide with hydrogen chloride. It has m. p.  $196^\circ$ , and its molecular weight in acetone corresponds to the formula  $\{\text{C}(\text{NPh})_2\}_3$ . The substance, which is called  *$\gamma$ -carbodiphenylimide*, does not revert to the unimolecular  $\alpha$ -carbodiphenylimide by heating, forms a *hydrochloride*,  $\text{C}_{39}\text{H}_{30}\text{N}_6\cdot\text{HCl}$ , m. p.  $207^\circ$ , *picrate*, m. p.  $157^\circ$ , and *aurichloride*,  $\text{C}_{39}\text{H}_{30}\text{N}_6\cdot\text{HAuCl}_4$ , decomposing at  $125^\circ$ , and by careful heating with alcohol and hydrochloric acid yields carbon dioxide, aniline, and Marekwald's pentaphenyldiguamide (Abstr., 1896, i, 29). The behaviour of the substance is best represented by the constitution of hexaphenylmelamine,  $\text{NPh}\cdot\text{C} \begin{array}{c} \text{NPh}\cdot\text{C}(\text{NPh}) \\ \text{NPh}\cdot\text{C}(\text{NPh}) \end{array} \text{NPh}$ .

C. S.

**Behaviour of Tribromophenol Towards Benzene in the Presence of Aluminium Chloride.** MORITZ KOHN and NOE L. MÜLLER (*Monatsh.*, 1909, 30, 407—409).—Bromobenzene and phenol are formed by the action of aluminium chloride on a solution of tribromophenol in benzene. Trichlorophenol under similar conditions remains unattacked.

W. H. G.

**Derivatives of 3:5-Dinitrophenol.** GUSTAV HELLER [with MAX KAMMANN] (*Ber.*, 1909, 42, 2191—2198).—3:5-Dinitrophenol is prepared by converting *s*-trinitrobenzene into dinitroanisole and hydrolysing this with concentrated sulphuric acid at  $140^\circ$  (Hantzsch, Abstr., 1907, i, 207). 3:5-Dinitrophenyl acetate,  $\text{C}_8\text{H}_6\text{O}_6\text{N}_2$ , crystallises from a mixture of benzene and light petroleum, and has m. p.  $126$ — $127^\circ$ ; the corresponding benzoate,  $\text{C}_{13}\text{H}_8\text{O}_6\text{N}_2$ , crystallises from alcohol in needles, m. p.  $130$ — $131^\circ$ . 3-Nitro-5-acetylaminophenol,  $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{NHAc}$ , obtained by reducing an acetic acid solution of the dinitrophenol with stannous chloride and hydrochloric acid, crystallises from ethyl acetate in yellow, microscopic prisms; it changes colour at  $240^\circ$ , decomposes at  $260^\circ$ , and is completely molten at  $270^\circ$ . When hydrolysed with hydrochloric acid, it yields Blanksma's 5-nitro-3-aminophenol (*Rec. trav. chim.*, 1892, 21, 254). An acetic acid solution of bromine reacts with the acetyl-amino-derivative, yielding

2-bromo-5-nitro-3-acetylaminophenol,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br}(\text{OH}) \cdot \text{NHAc}$ , which crystallises from ethyl acetate in yellow, pointed prisms, m. p. 242—243°. When hydrolysed with hydrochloric acid, 2-bromo-5-nitro-3-aminophenol,  $\text{C}_6\text{H}_5\text{O}_3\text{N}_2\text{Br}$ , is obtained, and separates from hot water or glacial acetic acid in reddish-brown crystals, m. p. 205°. The same compound can be obtained somewhat more readily by brominating nitroaminophenol with an acetic acid solution of bromine, but tribromo-5-nitro-2-aminophenol,  $\text{C}_6\text{H}_3\text{O}_3\text{N}_2\text{Br}_3$ , is also formed. The latter crystallises from light petroleum in yellow plates, m. p. 147°. The constitution of the 2-bromo-5-nitro-3-aminophenol follows from the fact that by the elimination of the amino-group a bromonitrophenol is obtained, which is identical with the 2-bromo-5-nitrophenol,  $\text{C}_6\text{H}_4\text{O}_3\text{NBr}$ , formed by the replacement of the amino-group in Friedlander and Zeitlin's 5-nitro-2-aminophenol (Abstr., 1894, i, 185). 2-Bromo-5-nitrophenol crystallises from light petroleum in colourless rods, m. p. 118—119°, and yields a benzoate,  $\text{C}_{13}\text{H}_8\text{O}_4\text{NBr}$ , which crystallises from alcohol in colourless needles, m. p. 127—128°.

3-Bromo-5-nitrophenol (Blanksma, *loc. cit.*) can be obtained by replacing the amino-group in 5-nitro-3-aminophenol by bromine. Its benzoate,  $\text{C}_{13}\text{H}_8\text{O}_4\text{NBr}$ , has m. p. 93—95°. 2-Bromo-5-acetylaminophenol,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NHAc}$ , obtained by reducing the 2-bromo-5-nitrophenol with stannous chloride and then treating with acetic anhydride, crystallises from aqueous acetic acid in colourless needles, m. p. 209—211°. When hydrolysed, it yields 2-bromo-5-aminophenol,  $\text{C}_6\text{H}_6\text{ONBr}$ , in the form of plates, m. p. 150° (decomp.). It has not been found possible to eliminate the amino-group from this compound.

4-Bromo-3-nitrophenol can be obtained by replacing the amino-group in Friedlander and Zeitlin's 3-nitro-4-aminophenol (Abstr., 1894, i, 185) by bromine (compare Lindner, Abstr., 1885, 774).

J. J. S.

**A New Method for the Alkylation of Phenols.** ALFRED EINHORN (*Ber.*, 1909, 42, 2237—2238).—The mixed carbonic esters of phenols lose carbon dioxide on heating, and pass into alkyl ethers of phenols:  $\text{Ar} \cdot \text{O} \cdot \text{CO} \cdot \text{OR} = \text{CO}_2 + \text{Ar} \cdot \text{O} \cdot \text{R}$ . The reaction is a general one, but does not proceed with equal readiness in all cases. The esters containing basic alkyl groups, such as guaiacol diethylaminoethyl carbonate, are completely converted after distilling once, or at most twice, in a vacuum, whilst  $\beta$ -naphthyl methyl carbonate requires thirty-six hours' boiling under atmospheric pressure. Secondary products are sometimes formed at the same time.

Guaiacol ethyl carbonate, when heated for seven days under atmospheric pressure, yields both guaiacol carbonate and guaiacol ethyl ether. The latter has b. p. 207—209° (Tiemann and Hoppe, Abstr., 1882, 54, give 213°).

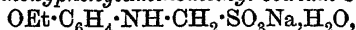
C. H. D.

**A New Formation of Esters by the Action of Chloro-carbonates on Acids.** JOHANNES HERZOG (*Ber.*, 1909, 42, 2557—2559. Compare Einhorn, preceding abstract).—Chloro-carbonic esters react with acids, eliminating carbon dioxide:

$R \cdot CO \cdot OH + Cl \cdot CO \cdot OR' = R \cdot CO \cdot OR' + HCl + CO_2$ , although the yield is only small. Unlike the chlorocarbonates of phenols obtained by Einhorn, the intermediate products in this case, the anhydrides,  $R \cdot CO \cdot O \cdot CO \cdot OR'$ , decompose at once.

The preparation of methyl benzoate and methyl cinnamate is described.  
C. H. D.

**Preparation of the Salts of *p*-Ethoxyphenylaminomethyl Sulphurous Acid.** ROBERTO LEPETIT (D.R.-P. 209695. Compare Knoevenagel, Abstr., 1904, i, 981; Bucherer and Schwalbe, Abstr., 1906, i, 828).—*p*-Ethoxyphenylaminomethyl sodium sulphite,

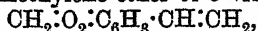


lustrous, white leaflets, is obtained by adding successively solutions of formaldehyde and sodium hydrogen sulphite to an alcoholic solution of *p*-phenetidine.

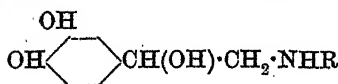
*p*-Ethoxyphenylaminomethyl hydrogen sulphite separates in white needles on acidifying the solution of the sodium salt. Its barium salt is sparingly soluble; its potassium and ammonium salts closely resemble the sodium derivative. The acid has interesting physiological properties, comparing favourably in this respect with phenacetin and lactophenin.  
F. M. G. M.

**Preparation of  $\alpha$ -3:4-Trihydroxyphenylethylamines.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 209609 and 209610).—Bases having the physiological properties of adrenaline may be produced by the following series of reactions.

$\beta$ -Chloro- $\alpha$ -hydroxy- $\alpha$ -3:4-methylenedioxyphenylethane, m. p. 95–96° (Barger, Trans., 1908, 93, 2083, gives 95°), is produced by adding chlorine to the methylene ether of 3-vinylcatechol,



and removing the  $\alpha$ -chlorine atom from the resulting dichloride with moist acetone. The chlorohydrin is then treated with phosphorus pentachloride; this replaces the methylene hydrogen by chlorine, yielding an unstable product, which when boiled with moist acetone gives rise to  $\beta$ -chloro- $\alpha$ -3:4-trihydroxy- $\alpha$ -phenylethane. This rather



unstable substance when treated with ammonia or primary amines yields the required bases, which have the annexed general formula, where R is

hydrogen or an alkyl group. The conversion of methylenedioxyphenylethylene dichloride,  $CH_2 : O_2 : C_6H_3 \cdot CHCl \cdot CH_2Cl$ , into (1)- $\beta$ -chloro- $\alpha$ -3:4-trihydroxyphenylethane can be effected in one operation by treating the former successively with phosphorus pentachloride and then with water.  
F. M. G. M.

**Naphthan- $\beta$ -diols.** HENRI LEROUX (*Compt. rend.*, 1909, 148, 1614–1616. Compare Abstr., 1904, i, 986; 1905, i, 278; this vol., i, 299).—The naphthan- $\beta$ -diols (decahydronaphthyl  $\beta$ -glycols) are obtained from dibromo-octahydronaphthalene under the same conditions as are required for the preparation of the tetrahydronaphthyl glycols (*cis*- and *trans*-). *cis*-Naphthan- $\beta$ -diol,  $C_{10}H_{18}O_2$ , crystallises in

slender needles or polygonal tablets, m. p. 160°; the *diacetate* forms large prisms, m. p. 85°; the *diphenylurethane* occurs in needles, m. p. 195°. *trans-Naphthan-β-diol* forms needles or prisms, m. p. 140°; its *diacetate* has not been obtained crystalline; its *diphenylurethane* forms fine needles, m. p. 121°. As in the case of the tetrahydronaphthyl glycols, a third isomeride exists, consisting of a compound of the *cis*- and *trans*-modifications; this is much more soluble than either of its generators, and has m. p. 125°. A similar *cis*+*trans*-compound, m. p. about 145°, exists in the case of the terpane diols. Bredt's compound, m. p. 96°, isomeric with *cis*- and *trans*-camphyl glycol, is probably of the same type (this vol., i, 498).  
W. O. W.

**Phenyl Sulphide.** ALFRED HIMMELBAUER (*Centr. Min.*, 1909, 396).—The refractive index of phenyl sulphide was found to be 1.635 for sodium light; by dissolving sulphur in the liquid the refractive index may be increased to 1.641. These values are considerably lower than that given in some text-books for this substance.  
L. J. S.

**Aromatic Homologues of *s*-Dichlorodimethyl Ether.** ALFRED KLIÉGL and KARL HAAS (*Ber.*, 1909, 42, 2581–2588).—The first aromatic homologue of *s*-dichlorodimethyl ether was obtained from *o*-nitrobenzaldehyde (Kliégel, Abstr., 1908, i, 82). Similar compounds are obtained by the action of phosphorus pentachloride on nitrobenzaldehydes without the presence of a solvent. Their reactions resemble those of the aliphatic homologues. When heated above the melting point they decompose into the nitrobenzaldehyde and nitrobenzylidene chloride.

*aa*-Dichloro-2 : 2'-dinitrobenzyl ether (*loc. cit.*) crystallises from xylene in colourless needles. Acetic anhydride and sodium acetate convert it into the *diacetoxy*-compound,  $[\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OAc})]_2\text{O}$ , leaflets, m. p. 171°.

*aa*-Dibromo-2 : 2'-dinitrobenzyl ether forms colourless, prismatic needles, decomp. 137–147°.

*aa*-Dichloro-3 : 3'-dinitrobenzyl ether, from *m*-nitrobenzaldehyde, crystallises from benzene in radiating bundles of prisms, m. p. 144°.

*aa*-Dichloro-4 : 4'-dinitrobenzyl ether, from *p*-nitrobenzaldehyde, separates from acetone in colourless rhombohedra, and from toluene in aggregates, m. p. about 170°.

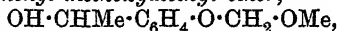
*aa*-Dibromo-4 : 4'-dinitrobenzyl ether has m. p. about 175°.

Hydrogen chloride in presence of phosphoryl chloride containing phosphoric acid converts *m*-nitrobenzaldehyde into *m*-nitrobenzylidene chloride.  
C. H. D.

**A Method of Applying the Grignard Reaction to Hydroxyaldehydes and Alkyl Hydroxycarboxylates.** PAUL HOERING and FRITZ BAUM (D.R.-P. 208886).—Hydroxyaldehydes and alkyl hydroxycarboxylates cannot be treated with the Grignard reagent, because the latter is decomposed by the free hydroxyl group. This result may be avoided by alkylating or acylating the hydroxyl group, but the former process has the disadvantage of yielding

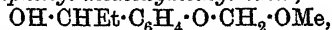
products which are only hydrolysed with difficulty, and the latter is rendered ineffectual because certain acyl residues, such as carbonyl or sulphonyl groups, inhibit the condensation. These difficulties have been overcome by employing the alkyl oxyalkyl ethers of the hydroxy-compounds. These groups are inert towards the Grignard reagent and are easily hydrolysed away from the product of the condensation, and in this way a series of secondary and tertiary aromatic alcohols has been obtained, which on account of their relatively slight toxicity and remarkably antiseptic properties have a distinct therapeutic value.

*o*-a-Hydroxyethylphenyl methoxymethyl ether,

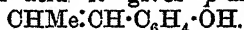


colourless, odourless liquid, b. p.  $141-143^\circ/12$  mm.,  $D^{19}_D$  1.065, is produced by adding an ethereal solution of *o*-methoxymethoxybenzaldehyde to a solution of methyl iodide and magnesium in dry ether. This compound, which is stable to alkali, is hydrolysed by alcoholic  $\text{H}_2\text{SO}_4$  with the formation of *o*-vinylphenol,  $\text{CH}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ .

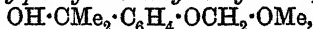
*p*-a-Hydroxypropylphenyl methoxymethyl ether,



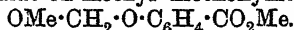
b. p.  $133-142^\circ/16$  mm., is similarly prepared from *p*-methoxymethoxybenzaldehyde,  $\text{OMe}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{COH}$ , and magnesium ethiodide. When hydrolysed with acid it gives *p*-anol,



*o*-a-Hydroxyisopropylphenyl methoxymethyl ether,

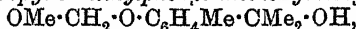


colourless liquid, b. p.  $143^\circ/15$  mm.,  $D^{17}_D$  1.083, results from the action of magnesium methiodide on methyl methoxymethoxybenzoate,

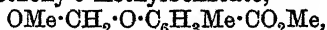


Hydrolysis of this product and distillation under ordinary pressure lead to the formation of *o*-propylenephénol,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}\cdot\text{CH}_2$ , a liquid with the odour of thymol, b. p.  $83^\circ/15$  mm.,  $D^{18}_D$  1.028.

*2*-a-Hydroxyisopropyl-5-methylphenyl methoxymethyl ether,

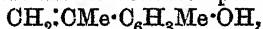


b. p.  $153-154.5^\circ/18$  mm.,  $D^{18}_D$  1.053, is produced by condensing methyl 2-methoxymethoxy-5-methylbenzoate,



with magnesium methiodide.

*6*-a-Hydroxyisopropyl-*m*-cresol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{C}_6\text{H}_3(\text{Me})\cdot\text{OH}$ , odourless, rhombic plates, m. p.  $62-63^\circ$ , is also formed in this reaction, and this, when distilled, yields the unsaturated phenol,



colourless liquid with odour of thymol, b. p.  $221-222^\circ/76$  mm.,  $D^{20}_D$  1.0065.

F. M. G. M.

**Preparation of Tertiary Aromatic Alcohols.** PAUL HOERING and FRITZ BAUM (D.R.-P. 208962).—Tertiary alcohols can be produced from the aromatic alkyl hydroxy-carboxylates or their alkali derivatives by treating these with excess (2–3 mols.) of magnesium alkyl halide.

An ethereal solution of magnesium ethyl bromide when added to the sodium derivative of methyl salicylate suspended in toluene and

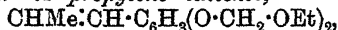
the mixture acidified with dilute acetic acid gives rise to *o*-*α*-hydroxy-isoamylphenol,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_2\text{Et}_2 \cdot \text{OH}$ , colourless needles, m. p. 55.5—56°, b. p. 151—152°/16 mm.

*4-α-Hydroxyisopropyl-m-cresol*,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$ , colourless, odourless, rhombic plates, m. p. 63°, is produced similarly by the interaction of methyl *m*-cresotate and magnesium methyl iodide. When magnesium ethyl iodide is employed in the foregoing condensation, then *4-α-hydroxyisoamyl-m-cresol*, colourless needles, m. p. 74—74.5°, is obtained. F. M. G. M.

**Preparation of Alkoxyethyl Ethers of Aromatic Hydroxy-compounds.** PAUL HOERING and FRITZ BAUM (D.R.-P. 209608).—The alkoxyethyl ethers of the aromatic hydroxy-compounds can be obtained by condensing the alkali derivatives of these substances with halogenated methyl alkyl ethers having the general formula  $\text{X} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{Alk}$ , where X is a halogen atom.

*Phenyl methoxyethyl ether*,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{OMe}$ , colourless liquid with fruity odour, b. p. 188—189°/760 mm., and  $D^{22}_D$  1.0270, is prepared by adding chloromethyl ether to an alcoholic solution of sodium phenoxide. The alkoxyethyl ethers of the cresols are similarly prepared. *p*-Nitrophenyl methoxyethyl ether,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{OMe}$ , crystals with sweet taste and pleasant odour, m. p. 24—25°, is prepared by adding chloromethyl ether to an alcoholic solution of sodium *p*-nitrophenoxide.

*iso*Eugenyl ethoxyethyl ether,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{CHMe}$ , when condensed with chloromethylethyl ether gives rise to the bisethoxyethyl ether of propylene catechol,



b. p. 187—191°/760 mm.

*o*-Methoxymethoxybenzaldehyde,  $\text{COH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{OMe}$ , b. p. 139—140°/11 mm. and 255—265°/760 mm.,  $D^{18}_D$  1.1450, is prepared by adding successively to finely divided sodium in toluene, alcohol and salicylaldehyde; the alcohol is then removed by distillation and chloromethyl ether is introduced.

*Methyl o-methoxymethoxybenzoate*, b. p. 154—155°/12 mm. and 270—273°/760 mm., is prepared by substituting methyl salicylate for salicylaldehyde in the preceding condensation; *o*-methoxymethoxybenzoic acid, needles, m. p. 64—65°, is obtained by alkaline hydrolysis.

F. M. G. M.

**Cotton-seed Oil, Especially the Unsaponifiable Constituents.** HERMANN MATTHES and W. HEINTZ (*Arch. Pharm.*, 1909, 247, 161—175).—Previous work on the unsaponifiable matter of cotton-seed oil has been confined to the solid portion, and this has been generally regarded as consisting of a single phytosterol (Bömer, *Abstr.*, 1899, ii, 191, 192, 259; Bömer and Winter, *Abstr.*, 1902, i, 30; ii, 184; and Heiduschka and Gloth, *Abstr.*, 1908, i, 883). In the present paper it is shown that the unsaponifiable matter consists of liquid oxygenated substances and a mixture of three solid phytosterols.

On saponification of the oil and extraction of the aqueous solution

with ether, 0.71% of unsaponifiable matter was obtained, in the form of a yellowish-brown mass, containing some crystals and having a pleasant odour. It was free from chlorine and sulphur (compare Wagner and Clement, *Zeit. Nahr-Genussm.*, 1909, 17, 266). On washing with light petroleum, the liquid portion passes into solution, leaving a residue, which on recrystallisation from alcohol yields first a minute quantity of a slightly yellow, flocculent substance, m. p. 81—82°, which does not absorb iodine, but gives characteristic colorations with the usual phytosterol reagents. The alcoholic mother liquor, on concentration, deposits a phytosterol,  $C_{27}H_{46}O, H_2O$ , m. p. 139°,  $[\alpha]_D - 23.14^\circ$  in alcohol and ether, which is apparently identical with that described by Bömer and others; the acetate has  $[\alpha]_D - 21.42^\circ$  in alcohol and ether.

The solution in light petroleum, referred to above, was concentrated and cooled in a freezing mixture. This caused the separation of a colourless substance,  $C_{10}H_{16}O$ , m. p. 172—180°,  $[\alpha]_D + 36.7^\circ$  in alcohol, which crystallises best from acetone. It gives characteristic colorations with the usual phytosterol reagents, and absorbs iodine.

The liquid portion of the unsaponifiable matter remains in the light petroleum mother liquor, and, after removal of the solvent, was separated into five portions by fractional distillation. None of these boiled constantly. All the fractions contained oxygenated substances, but were free from nitrogen. The fractions gave characteristic colorations with the usual phytosterol reagents, and absorbed iodine.

T. A. H.

**Reduction of *o*-Nitrobenzoic Acid and its Esters.** EUGEN BAMBERGER and FRANK LEE PYMAN (*Ber.*, 1909, 42, 2297—2330).—Pure *o*-hydroxylaminobenzoic acid,  $OH \cdot NH \cdot C_6H_4 \cdot CO_2H$ , m. p. 142.5° (decomp.) (119°: Kalle & Co., D.R.-P. 89978), is obtained by adding ammonium chloride to an aqueous solution of barium *o*-nitrobenzoate at 10°, and then gradually zinc dust, the temperature being kept below 20° and air excluded; the mixture is filtered, and the filtrate treated with 25% hydrochloric acid at 0°; the precipitate, which is almost white in the absence of light, is dried and purified by precipitating its warm alcoholic solution with warm chloroform in the dark, and finally crystallising from ether to free it from *o*:*o'*-azoxybenzoic acid. *o*-Hydroxylaminobenzoic acid separates from ether in white needles, and has the general properties of the  $\beta$ -aryl-hydroxylamines. It is amphoteric, and is oxidised by alkalis in the air. Nitrous acid at -10° converts it into nitroso-*o*-carboxyphenyl-hydroxylamine, or, in excess, into a diazonium salt. It is oxidised by alcoholic ferric chloride to *o*-nitrosobenzoic acid, and condenses with the latter in alcohol to form *o*:*o'*-azoxybenzoic acid. At the ordinary temperature air-free 10% alcoholic potassium hydroxide converts it into *o*:*o'*-azoxybenzoic acid, *o*-nitrobenzoic acid, and anthranilic acid. Boiling water, free from oxygen, converts it into *o*:*o'*-azoxybenzoic acid and 6-amino-3-hydroxybenzoic acid. Boiling 2*N*-sulphuric acid also forms the aminohydroxybenzoic acid, but acts mainly as a dehydrating agent, giving the anhydride,  $C_7H_5O_2N$ , which

is also produced by 50% sulphuric acid at the ordinary temperature, and is shown in the sequel to be benzisooxazolone.

*Ethyl o-hydroxylaminobenzoate*,  $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH}$ , m. p.  $78.5^\circ$ , softening at  $75.5^\circ$ , is obtained by shaking ethereal ethyl *o*-nitrobenzoate and aqueous ammonium chloride with zinc dust for two hours at the ordinary temperature; by-products of the reduction are benzisooxazolone, ethyl anthranilate, and ethyl *o*:*o'*-azoxybenzoate. Ethyl *o*-hydroxylaminobenzoate is precipitated from its chloroform solution by light petroleum in long needles, is soluble in mineral acids, reduces copper acetate and silver nitrate, is oxidised to ethyl *o*-nitrosobenzoate by ferric chloride, and to ethyl *o*-nitrobenzoate by potassium dichromate and sulphuric acid, and yields the nitrosoamine and a diazonium salt by treatment with nitrous acid. It differs from other  $\beta$ -arylhydroxylamines in not reducing Fehling's solution and in its behaviour with alkalis. Whilst solutions of  $\beta$ -arylhydroxylamines are rendered turbid by alkalis owing to more rapid atmospheric oxidation, ethyl *o*-hydroxylaminobenzoate forms a clear, orange-yellow solution in dilute sodium hydroxide, which quickly turns yellow, and by acidification yields a white, crystalline precipitate of benzisooxazolone.

*Methyl o-hydroxylaminobenzoate* has been obtained in a similar manner as a brownish-yellow oil, possessing properties similar to those of the ethyl ester.

*Benzisooxazolone*,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NH} \\ \text{CO}\end{smallmatrix}\rangle\text{O}$ , m. p.  $112^\circ$  (decomp.), crystallises in colourless needles, forms solutions which quickly turn red, and is not more soluble in acids than in water. It reddens litmus and dissolves in alkalis, ammonium hydroxide, and sodium carbonate. It does not reduce boiling Fehling's solution, can be reduced to anthranilic acid, is oxidised by aqueous alcoholic ferric chloride, giving an indigo-blue solution, becoming green and then turbid, and when heated, alone or in boiling water, is converted into *o*:*o'*-azobenzoic acid. When treated with acetyl chloride, it forms 2-acetylbenzisooxazolone,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NAc} \\ \text{CO}\end{smallmatrix}\rangle\text{O}$ , m. p.  $117.5\text{--}118.5^\circ$ , identical with the by-product obtained by Ciamician and Silber (Abstr., 1901, i, 548; 1902, i, 378) during the interaction of paraldehyde and *o*-nitrobenzaldehyde; the same substance is produced by heating *o*-nitrosobenzoic acid with paraldehyde. The last reaction, in view of the interaction of nitrosobenzene and formaldehyde to yield the compound  $\text{OH}\cdot\text{NPh}\cdot\text{CHO}$  (Abstr., 1902, i, 279), leaves little doubt as to the constitution of 2-acetylbenzisooxazolone; the constitution is supported by the reduction of the substance to *N*-acetylanthranilic acid by aluminium foil and water. 2-Benzoylbenzisooxazolone,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NBz} \\ \text{CO}\end{smallmatrix}\rangle\text{O}$ , m. p.  $153\text{--}154^\circ$ , is obtained by the Schotten-Baumann method.

2-Ethylbenzisooxazolone, obtained by heating alcoholic benzisooxazolone with ethyl iodide and sodium ethoxide, is an oil,  $D_{20}^{25} 1.164$ , which is volatile with steam, is reduced to *N*-ethylanthranilic acid by zinc and sulphuric acid, and is insoluble in acids. Its solution in sodium hydroxide yields by acidification *N*-ethyl-*o*-hydroxylaminobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{OH}$ , m. p.  $100.5^\circ$ , which reduces

Fehling's solution, is oxidised to *o*-nitrosobenzoic acid by alkaline potassium permanganate, and is soluble in acids, the solution, however, depositing shortly the original 2-ethylbenzisooxazolone. 2-Methylbenzisooxazolone, D<sup>24</sup> 1.398, behaves like the ethyl ether, and is obtained in a similar manner.

Benzisooxazolone itself may be either  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} O$  or  $C_6H_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \end{smallmatrix} O$ . The alkali salts are probably of the latter type; benzisooxazolone has the former constitution, which is supported by the great similarity in the method of formation and the behaviour of the substance to Claisen's monocyclic isooxazolones. C. S.

**Acylation of Amines.** HARTWIG FRANZEN (*Ber.*, 1909, 42, 2465—2468).—A convenient method of acylating amino-derivatives of benzene consists in suspending the hydrochloride of the base in benzene, adding rather more than the theoretical amount of benzoyl or other acid chloride, and heating on the water-bath in a reflux apparatus until hydrogen chloride is no longer evolved. The acyl derivative separates as the solution cools, or may be obtained after removal of the benzene. Benzoyl derivatives of aniline, dibenzylamine, glycine ester, phenylhydrazine, phenylbenzylhydrazine, and hydroxylamine; *m*-nitrobenzoyl derivatives of aniline, glycine ester, and phenylbenzylhydrazine, and *p*-methoxybenzoyl derivatives of glycine ester and phenylbenzylhydrazine have been prepared by this method.

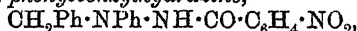
When aniline hydrochloride and acetic anhydride are heated at 130—140° for an hour, acetanilide is obtained.

*Benzoyldibenzylamine*,  $\text{COPh} \cdot \text{N}(\text{CH}_2\text{Ph})_2$ , crystallises from alcohol in small, colourless needles, m. p. 112—113°.

*Ethyl m-nitrobenzoylglycine*,  $\text{NO}_2 \cdot C_6H_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , crystallises from water in colourless needles, m. p. 75°.

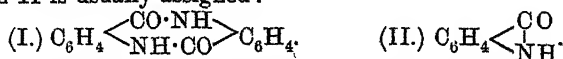
*Ethyl p-methoxybenzoylglycine*,  $\text{OMe} \cdot C_6H_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , crystallises from alcohol in slender, colourless needles, m. p. 98—99°.

*m-Nitrobenzoyl- $\alpha$ -phenylbenzylhydrazine*,



crystallises from alcohol in pale yellow needles, m. p. 137°. *p-Methoxybenzoyl- $\alpha$ -phenylbenzylhydrazine*,  $C_{21}H_{20}O_2N_2$ , crystallises from alcohol in slender needles, m. p. 177°. J. J. S.

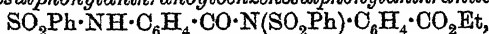
**Bimolecular Anhydrides of Anthranilic Acid.** GEORG SCHROETER and O. EISLEB (*Annalen*, 1909, 367, 101—168. Compare *Abstr.*, 1907, i, 529, 620).—The object of this investigation was to obtain information on the behaviour of *o*-aminocarboxylic acids of the aromatic series in the formation of cyclic amides; further, to prepare a bimolecular anhydride of anthranilic acid having the formula I in order to compare it with anthranil, to which the constitution II is usually assigned:



I. Preparation of *s*-Dianthranilides with a Negative Substituent

attached to the Nitrogen.—Derivatives of anthranilic acid of the type  $\text{NHX} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$  yield the corresponding chlorides on treatment with phosphorus pentachloride when X is a negative substituent such as arylsulphonyl, dinitrophenyl, or trinitrophenyl. The chlorides are converted into the corresponding dianthranilides by treating their solutions in pyridine with alcohol, water, or dilute acid.

Benzenesulphonylanthranilic chloride (Abstr., 1907, i, 529) is converted by methyl alcohol into methyl benzenesulphonylanthranilate,  $\text{C}_{14}\text{H}_{13}\text{O}_4\text{NS}$ , m. p.  $107^\circ$ . Dibenzene sulphonyldianthranilide (*loc. cit.*) is obtained in quantitative yield from the chloride by the method just described; it is decomposed (1) by hot, aqueous sodium hydroxide into benzenesulphonylanthranilic acid; (2) by alcoholic ammonia into benzenesulphonylanthranilamide; (3) by sodium ethoxide in alcohol into ethyl benzenesulphonylanthranoylbenzenesulphonylanthranilate,



a crystalline substance, m. p.  $201-202^\circ$ .

p-Toluenesulphonylanthranilic chloride,  $\text{C}_{14}\text{H}_{12}\text{O}_3\text{NSCl}$ , forms compact crystals, m. p.  $128-129^\circ$ , and is converted by ethyl alcohol into ethyl p-toluenesulphonylanthranilate,  $\text{C}_{16}\text{H}_{17}\text{O}_4\text{NS}$ , m. p.  $112^\circ$ . Di-p-toluenesulphonyldianthranilide,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Me}) \\ \text{CO} \cdot \text{N}(\text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{Me}) \end{smallmatrix} \right\rangle \text{C}_6\text{H}_4$ , has m. p.  $240^\circ$ , and crystallises with chloroform of crystallisation.

$\beta$ -Naphthalenesulphonylanthranilic acid,  $\text{C}_{17}\text{H}_{13}\text{O}_4\text{NS}$ , formed by the interaction of anthranilic acid and  $\beta$ -naphthalenesulphonyl chloride in benzene, has m. p.  $223^\circ$ ; the chloride,  $\text{C}_{17}\text{H}_{12}\text{O}_3\text{NSCl}$ , has m. p.  $132^\circ$ ; the ethyl ester crystallises in white needles, m. p.  $131.5^\circ$ . Di- $\beta$ -naphthalenesulphonyldianthranilide,  $\text{C}_{34}\text{H}_{22}\text{O}_6\text{N}_2\text{S}_2$ , has m. p.  $254-255^\circ$ , and crystallises with  $1\text{CHCl}_3$ .

2:4-Dinitrophenylanthranilic chloride,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ , forms compact, orange crystals, m. p.  $179^\circ$  (decomp.). Ethyl 2:4-dinitrophenylanthranilate has m. p.  $164-166^\circ$ . 1:3-Dinitroacridone,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} \right\rangle \text{C}_6\text{H}_2(\text{NO}_2)_2$ , is formed by heating 2:4-dinitrophenyl-

anthranilic acid in phosphorus oxychloride with phosphorus pentachloride; it crystallises in yellowish-brown leaflets, m. p. above  $300^\circ$ . Bis-2:4-dinitrophenyldianthranilide,  $\text{C}_{26}\text{H}_{14}\text{O}_{10}\text{N}_2$ , is a pale yellow powder which decomposes without melting when heated; it is converted by alcoholic ammonia under pressure at  $100^\circ$  into 2:4-dinitrophenylanthranilamide,  $\text{C}_{13}\text{H}_{10}\text{O}_5\text{N}_4$ , orange-yellow needles, m. p.  $248^\circ$ .

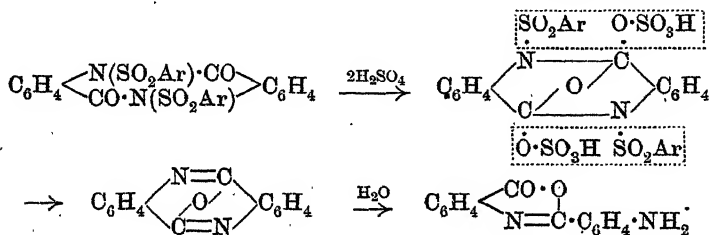
Picrylanthranilic chloride,  $\text{C}_{13}\text{H}_7\text{O}_7\text{N}_4\text{Cl}$ , crystallises in yellow needles, m. p.  $224-225^\circ$  (decomp.), and is converted by boiling with nitrobenzene into 1:3-dinitroacridone, the amide,  $\text{C}_{13}\text{H}_6\text{O}_7\text{N}_5$ , forms deep red crystals, and decomposes before melting; the ethyl ester,  $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ , crystallises in yellow needles, m. p.  $169^\circ$ . Dipicryldianthranilide,  $\text{C}_{26}\text{H}_{12}\text{O}_{14}\text{N}_8$ , crystallises in lemon-yellow needles, m. p. above  $200^\circ$  (decomp.).

II. Anthranoylanthranilic Acids and their O-Anhydrides. Structure of the So-called Acylanthranils.—Anthranoylanthranilic acid when treated with thionyl chloride yields an anhydride (compare Schroeter, Abstr., 1907, i, 529), which is also formed by the action of concentrated sulphuric acid on dibenzene sulphonyldianthranilide. It is shown that this substance is not dianthranilide, but an o-amino-derivative of the

so-called benzoylanthranil. Two formulæ have been suggested for the latter substance, namely: (I)  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NBz} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$  and (II)  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}=\text{CPh} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{smallmatrix}$ ; the second must, however, be the correct one for the following reason.

All *N*-carbacylanthranilic acids capable of reacting as iminohydrins,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{CR} \cdot \text{OH}$ , readily pass into unimolecular anhydrides, which must consequently have constitutions analogous to II; on the other hand, *N*-anthranilic acid derivatives with negative substituents, such as arylsulphonyl and polynitrophenyl, which do not exist in the enolic form, yield bimolecular anhydrides, namely, the dianthranilides. The yellow anhydride obtained from anthranoylanthranilic acid has therefore the formula  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \end{smallmatrix}$ , or more probably

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \end{smallmatrix}$ , since the salts are colourless. The formation of the anhydride from diarylsulphonyldianthranilides by the action of sulphuric acid, for reasons given in III, is represented as follows:



*o*-Nitrobenzoylanthranilic-*O*-anhydride,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \end{smallmatrix}$ , prepared by the action of thionyl chloride on *o*-nitrobenzoylanthranilic acid, crystallises in colourless needles, m. p. 197°; attempts to reduce it to anthranoylanthranilic-*O*-anhydride were successful.

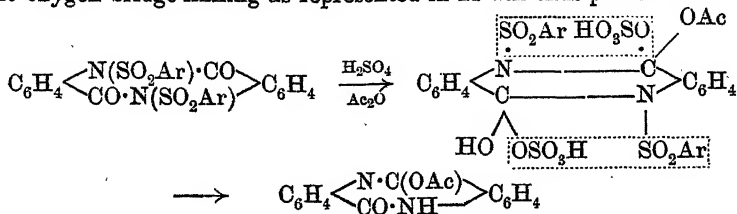
The presence of the amino-group in anthranoylanthranilic-*O*-anhydride was shown (1) by conversion into the *hydroxyazo*-derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \end{smallmatrix}$ , crystallising in red needles; (2) by combination with 1:2-naphthaquinone-4-sulphonic acid, yielding the substance,  $\text{C}_6\text{H}_6 \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N}=\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{O} \end{smallmatrix}$ , a dark red, crystalline powder.

Benzenesulphonylanthranilic-*O*-anhydride (compare Schroeter, Abstr., 1907, 620) may be prepared (1) by the action of thionyl chloride on benzenesulphonylanthranilic acid; (2) by treating anthranoylanthranilic-*O*-anhydride with benzenesulphonyl chloride; (3) by acting on anthranil with benzenesulphonyl chloride; (4) by the interaction of anthranil and benzenesulphonylanthranilic chloride; (5) when benzenesulphonylanthranilic acid is heated with phosphorus pentachloride at 140–160°.

III. *Dianthranilide and its Derivatives*.—Attempts to prepare simple derivatives of dianthranilide by the following methods were

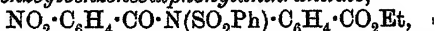
unsuccessful: (1) hydrolysis and reduction of ethyl *o*-nitrobenzoylbenzenesulphonylanthranilate; (2) reduction of *o*-nitrobenzoylmethylanthranilic acid; (3) elimination of water from anthranoylphenylanthranilic acid.

An acetate of dianthranilide was finally obtained by treating an arylsulphonyldianthranilide with sulphuric acid in the presence of acetic anhydride; the formation of the intermediate compound with the oxygen-bridge-linking as represented in II was thus prevented:



The acetyl derivative is readily converted by alkalis into dianthranilide.

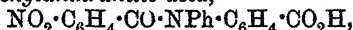
*Ethyl o*-nitrobenzoylbenzenesulphonylanthranilate,



prepared by the action of *o*-nitrobenzoyl chloride on ethyl sodiobenzenesulphonylanthranilate, has m. p. 137°.

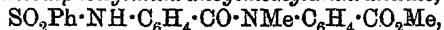
*Methyl methylantranilate* is a liquid, b. p. 256°/760 mm., 128°/13 mm.; it reacts with *o*-nitrobenzoyl chloride, forming *methyl o*-nitrobenzoylmethylanthranilate, colourless prisms, m. p. 117°, which when hydrolysed yields the acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 216°.

*o*-Nitrobenzoylphenylanthranilic acid,

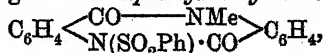


prepared from phenylanthranilic acid and *o*-nitrobenzoyl chloride, crystallises with 1Me·OH or 1Et·OH in yellow needles, m. p. 178—179°. The *methyl ester*,  $\text{C}_{21}\text{H}_{16}\text{O}_5\text{N}_2$ , can only be prepared by the action of methyl iodide on the *silver salt*; it has m. p. 174°. The acid is reduced by titanous chloride to *anthranoylphenylanthranilic acid*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , crystallising in pale yellow needles, m. p. 227° (decomp.).

*Methyl benzenesulphonylanthranoylmethylanthranilate*,



is formed by the interaction of benzenesulphonylanthranilic chloride and methyl methylantranilate; it has m. p. 125°. The *ethyl ester*, prepared similarly, has m. p. 133°. The acid,  $\text{C}_{22}\text{H}_{18}\text{O}_5\text{N}_2\text{S}$ , has m. p. 207°, and is converted by cold concentrated sulphuric acid into *anthranoylmethylanthranilic acid*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , compact, yellow crystals, m. p. 170° (very heated quickly); the *copper salt* forms olive-green needles. Benzenesulphonylanthranoylmethylanthranilic acid is converted by thionyl chloride into the *chloride*,  $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N}_2\text{S} \cdot \text{SOCl}_2$ , a colourless powder, which is acted on by pyridine, yielding *benzenesulphonylmethylidanthranilide*,



obtained as a white, crystalline powder, m. p. 212°. The latter substance when treated with cold concentrated sulphuric acid yields

*methylanthranilide*,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{NMe} \\ \text{NH} - \text{CO} \end{smallmatrix} C_6H_4$ , crystallising in white needles, m. p.  $259^\circ$ , which with methyl sulphate and aqueous sodium hydroxide yields *dimethylanthranilide*,  $C_6H_4 \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{CO} \cdot \text{NMe} \end{smallmatrix} C_6H_4$ , crystallising in large, transparent, colourless prisms.

*Acetylthranilide*,  $C_6H_4 \begin{smallmatrix} \text{CO} - \text{NH} \\ \text{N} : \text{C}(\text{OAc}) \end{smallmatrix} C_6H_4$  (?), crystallises in small, colourless needles, and decomposes above  $280^\circ$ ; it is converted by acetyl chloride in quinoline or acetic anhydride in pyridine into a substance, m. p. about  $200^\circ$ .

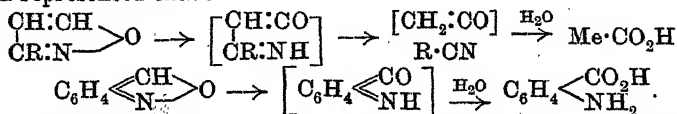
*Dianthranilide*,  $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} C_6H_4$ , crystallises in colourless needles, m. p.  $330^\circ$  (decomp.); the *silver* salt is a white powder; the *sodium* salt,  $C_{14}H_8O_2N_2Na_2$ , crystallises with  $2\text{Et} \cdot \text{OH}$ , and is converted (1) by methyl sulphate into methylthranilide, (2) by benzenesulphonyl chloride into dibenzenesulphonyldianthranilide, (3) by  $\beta$ -naphthalenesulphonyl chloride into di- $\beta$ -naphthalenesulphonyldianthranilide.

IV. *Conclusions*—(a) *Fission of Arylsulphonylanilides by Sulphuric Acid*.—The method adopted in this investigation for the elimination of arylsulphonyl groups, namely, by the action of cold concentrated sulphuric acid, is shown to be generally applicable. Thus, ethyl benzenesulphonylanthranilate is converted into ethyl anthranilate, similarly with the corresponding acid; benzenesulphonanilide yields sulphanilic acid.

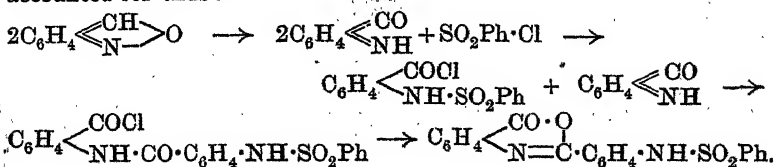
(b) *Relationship between the Formulae of Dianthranilide, Anthranil, and Derivatives of Anthranilic Acid*.—Arguments are advanced in favour of representing anthranil as 3:4-benzisoxazole,



Claisen has shown (Abstr., 1904, i, 14) that 3:5-dialkylisoxazoles are far more stable than 3- or 5-alkylisoxazoles, in agreement with which, methylanthranil, corresponding with the former class of compounds, is far more stable towards alkali than anthranil (compare Bamberger, Abstr., 1904, i, 422). The analogy between the decomposition of 3-alkylisoxazolones and anthranil by alkalis is striking when represented thus:

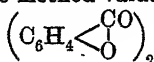


The formation of benzenesulphonylanthranoylanthranilic-*O*-anhydride by the action of benzenesulphonyl chloride on anthranil is readily accounted for thus:



In agreement with this assumption is the fact that an 80% yield of the anhydride is obtained by the action of benzenesulphonylanthranilic chloride on anthranil (1 mol.).

(c) *Comparison of Dianthranilide with the Di- and Poly-salicylides.*—Mol. wt. determinations of Anschütz's chloroform-salicylide (Abstr., 1893, i, 165) in phenol and nitrobenzene by the cryoscopic method give values corresponding with  $(C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix})_4$ , whilst in nitrobenzene by the ebullioscopic method values agreeing with



are obtained.

It is considered probable that this salicylide, obtained by the action of phosphoryl chloride on salicylic acid, is a polymeride of  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix}$ , existing as  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} C \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix} C_6H_4$ ,  $(C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix})_3$ , etc., according to the nature of solvent, temperature, etc. The disalicylide of Einhorn and Pfeiffer (Abstr., 1901, i, 712), on the contrary, is probably structurally analogous to dianthranilide,  $C_6H_4 \begin{smallmatrix} \diagup CO \cdot O \\ \diagdown O \cdot CO \end{smallmatrix} C_6H_4$ .

W. H. G.

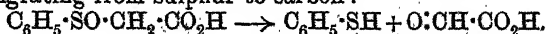
**Bromides of Arylthioglycollic [Arylthiolacetic] Acids.** RUDOLF PUMMERER (*Ber.*, 1909, 42, 2275—2282).—Arylthiolacetic acids are capable of taking up two atoms of bromine in carbon disulphide to form crystalline dibromides.

*Phenylthiolacetic acid dibromide*,  $C_6H_5 \cdot SBr_2 \cdot CH_2 \cdot CO_2H$ , crystallises from carbon disulphide in groups of golden-yellow prisms. It turns moist potassium iodide-starch paper blue. Alcohol converts it into ethyl phenylthiolacetate and brominated esters. The dibromide changes, especially on heating, into the *p*-bromo-acid, which may be converted by the action of chlorosulphonic acid, followed by the removal of bromine by alkali and zinc dust, into thioindigotin.

*p-Tolylthiolacetic acid monobromide*, which is the chief product of the action of bromine on the acid, behaves as a double compound of the dibromide with the acid,  $C_7H_7 \cdot SBr_2 \cdot CH_2 \cdot CO_2H, C_7H_7 \cdot S \cdot CH_2 \cdot CO_2H$ . It crystallises in thick plates or prisms, m. p.  $82^\circ$ , which are yellow by transmitted, but scarlet by reflected, light, with a bluish-red reflex. The *dibromide*, obtained from the mother liquor, forms thin, yellow plates, decomp.  $70^\circ$ . It is capable of taking up more bromine, but a definite compound could not be isolated.

C. H. D.

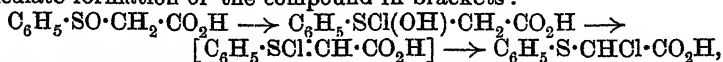
**Phenylsulphoxyacetic Acid.** RUDOLF PUMMERER (*Ber.*, 1909, 42, 2282—2291).—*Phenylsulphoxyacetic acid* is obtained either by hydrolysing phenylthiolacetic acid dibromide (preceding abstract), or by oxidising phenylthiolacetic acid with hydrogen peroxide. It crystallises from ethyl acetate in prisms, m. p.  $116^\circ$ . Even traces of mineral acids decompose it into thiophenol and glyoxylic acid, the oxygen migrating from sulphur to carbon:



This reaction takes place even in presence of hydriodic acid, or on heating alone. Dilute aqueous solutions are stable.

Concentrated hydrobromic acid forms the bromophenyl acid. Hydrogen chloride, on the other hand, forms *α-chloro-α-phenylthiol-acetic acid*,  $C_6H_5 \cdot S \cdot CHCl \cdot CO_2H$ , m. p. 69—72°, which decomposes readily, forming thiophenol. The *ethyl* ester is an oil, b. p. 158—160°/14.5 mm., which readily loses chlorine. Phenyl and benzyl sulphoxides also absorb hydrogen chloride, forming oils, which appear to be labile hydrochlorides. These sulphoxides, like phenylsulphoxyacetic acid, give intense blue colorations with fuming sulphuric acid.

The reaction with hydrogen chloride may occur through the intermediate formation of the compound in brackets :

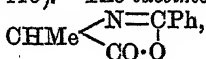


and a similar reaction may be assumed for the formation of thiophenol by acids.

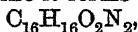
The dynamic isomerism of the sulphoxides assumed by Smythe (Trans., 1909, 95, 349) is unlikely, since the tendency of quadrivalent sulphur to become bivalent is not likely to be reversible.

C. H. D.

**Lactimones of Benzoylalanine and of Benzoylphenylalanine.** ERNST MOHR and FRITZ STROSCHEIN (*Ber.*, 1909, 42, 2521—2523. Compare Abstr., 1907, i, 415).—The *lactimone* of benzoylalanine,

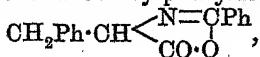


m. p. 39°, is obtained by heating benzoylalanine with acetic anhydride and fractionally distilling at 0.2 to 0.5 mm. With water, ammonia, and alcohol, it yields benzoylalanine and its amide and ethyl ester respectively, whilst with aniline it forms benzoylalanineanilide,



m. p. 175°. In ethereal solution the lactimone adds on hydrogen chloride to form *benzoylalanyl chloride*,  $COPh \cdot NH \cdot CHMe \cdot COCl$ , a white powder, which decomposes at 125°, and reacts with *α-aminoisobutyric acid* in aqueous, faintly alkaline solution to form *benzoylalanyl-α-aminoisobutyric acid*,  $COPh \cdot NH \cdot CHMe \cdot CO \cdot NH \cdot CMe_2 \cdot CO_2H$ , m. p. 199°, which, when warmed with acetic anhydride, yields the *lactimone*,  $COPh \cdot NH \cdot CHMe \cdot C \begin{array}{c} \diagup \text{N} \cdot CMe_2 \\ \diagdown \text{O} \cdot \text{CO} \end{array}$ , b. p. 138°/0.2—0.5 mm.,

m. p. 116°. The *lactimone* of benzoylphenylalanine,



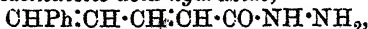
obtained from hippuric acid, has m. p. 71°, and reacts with water, alcohol, ammonia, aniline, and hydrogen chloride in a similar manner to the lactimone of benzoylalanine.

C. S.

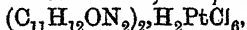
**Additive Capacity of Unsaturated Organic Acids and their Esters.** ADOLF RIEDEL and ERNST SCHULZ (*Annalen*, 1909, 367, 14—39. Compare Posner and Oppermann, Abstr., 1907, i, 55; Posner, *ibid.*, 212; Riedel, Abstr., 1908, i, 536).—An investigation on the

behaviour of acids with conjugated ethylene linkings towards hydrazine, phenylhydrazine, and hydroxylamine. It is found that the tendency of these acids to form additive compounds with the reagents mentioned varies largely with the nature of the acid and the addendum; rules of general applicability cannot be deduced. Attempts to combine toluenesulphonic acid, sulphur dioxide, potassium sulphite, and hydrogen chloride with cinnamylideneacetic acid and sorbic acid were unsuccessful.

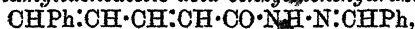
Cinnamylideneacetic acid yields with hydrazine hydrate the *hydrazine* salt,  $C_{11}H_{14}O_2N_2$ , crystallising in glistening, white leaflets, m. p.  $140^\circ$  (decomp.). The ethyl ester, however, reacts with hydrazine hydrate, yielding *cinnamylideneacetic acid hydrazide*,



which crystallises in long, slender, white needles, m. p.  $155^\circ$ ; the *sodium* salt,  $C_{11}H_{11}ON_2Na$ , is a reddish-yellow powder, which crepitates when heated; the *hydrochloride*,  $C_{11}H_{12}ON_2HCl$ , crystallises in colourless leaflets and decomposes at about  $195^\circ$ ; the *platinichloride*,

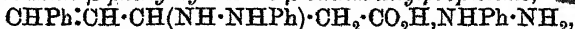


is a yellowish-brown powder; the *ovalate*,  $C_{24}H_{26}O_6N_4 \cdot 4H_2O$ , forms white, glistening leaflets, m. p.  $270^\circ$ ; the *picrate*,  $C_{17}H_{15}O_8N_5$ , crystallises in prismatic, coppery-red, glistening leaflets, m. p.  $98-99^\circ$  (decomp.). The parent substance is converted by bromine in *carbon tetrachloride* into *α,β,γ,δ-tetrabromo-δ-phenylvaleric acid hydrazide*,  $C_{11}H_{12}ON_2Br_4$ , obtained as small, white crystals, m. p.  $170^\circ$  (decomp.). The following compounds are prepared by treating the hydrazide with the necessary aldehyde. *Cinnamylideneacetic acid benzylidenehydrazide*,



stellate groups of sulphur-yellow needles, m. p.  $207^\circ$ ; *isopentylidene* derivative,  $C_{11}H_{16}O \cdot NH \cdot N:CH \cdot C_4H_9$ , slender, white needles, m. p.  $158^\circ$ ; *p-tolylidene* derivative,  $C_{11}H_{15}O \cdot NH \cdot N:CH \cdot C_6H_4Me$ , slender, sulphur-yellow needles, m. p.  $204^\circ$ ; *o-hydroxybenzylidene* derivative,  $C_{18}H_{16}O_2N_2$ , felted, slender, yellow needles, m. p.  $232^\circ$ ; *p-methoxybenzylidene* derivative, slender, yellow needles, m. p.  $203^\circ$ ; *m-nitrobenzylidene* derivative,  $C_{18}H_{15}O_2N_3$ , golden-yellow needles, m. p.  $204^\circ$ ; *4-hydroxy-3-methoxybenzylidene* derivative,  $C_{19}H_{18}O_3N_2$ , golden-yellow needles, m. p.  $225^\circ$ ; *cinnamylidene* derivative,  $C_{20}H_{18}ON_2$ , slender, golden-yellow needles, m. p.  $236^\circ$ . *Cinnamylideneacetic acid acethydrazide*,  $C_{10}H_9 \cdot CO \cdot NH \cdot NHAc$ , prepared by the action of acetic anhydride on the parent substance, forms small, yellowish-white crystals, m. p.  $214^\circ$  (decomp.). The corresponding *benzhydrazide*,  $C_{10}H_9 \cdot CO \cdot NH \cdot NHBz$ , crystallises in silvery, white, prismatic leaflets, m. p.  $212^\circ$ . The *semicarbazide*,  $C_{10}H_9 \cdot CO \cdot NH \cdot NH \cdot CO \cdot NH_2$ , crystallises in faintly yellow leaflets, m. p.  $164^\circ$  (decomp.).

Cinnamylideneacetic acid reacts with phenylhydrazine, yielding *phenylhydrazine β-phenylhydrazino-β-cinnamenylpropionate*,



which forms small, yellow, crystalline nodules, m. p.  $160^\circ$  (decomp.); the *dibromide*,  $C_{23}H_{26}O_2N_4Br_2$ , forms small, granular crystals, m. p. about  $150^\circ$  (decomp.).

*Hydroxylamine cinnamylideneacetate*,  $C_{10}H_9 \cdot CO_2H \cdot NH_2 \cdot OH$ , is obtained by the action of hydroxylamine on the acid as compact,

colourless crystals, decomposing at 135°. When the methyl ester is treated with hydroxylamine it yields *hydroxylamine β-hydroxylamino-β-cinnamenylpropionylhydroxamate*,

$\text{CHPh}:\text{CH}:\text{CH}(\text{NH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{OH}, \text{NH}_2\cdot\text{OH}$ , obtained as yellow crystals which decompose at 120—130°. The *acid*,  $\text{C}_{11}\text{H}_{14}\text{O}_3\text{N}_2$ , prepared by heating a solution of the hydroxylamine salt in methyl alcohol, forms small, granular, white crystals, and decomposes at 131—133°; the *tetrabenzoyl* derivative,  $\text{C}_{39}\text{H}_{30}\text{O}_7\text{N}_2$ , crystallises in glistening, long, white, prismatic needles, m. p. 167—168°. The hydroxamic acid is converted by ammoniacal silver nitrate into *γ-cinnamenylisooxazolone*,  $\text{C}_{11}\text{H}_9\text{O}_2\text{N}$ , obtained as a reddish-brown, sandy powder, decomposing at 90°.

Sorbyl chloride reacts with phenylhydrazine in ethereal solution, yielding *sorbic acid phenylhydrazide*,  $\text{CH}_3\cdot[\text{CH}]_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ , pearly leaflets, m. p. 162—163°, and with *o*-toluidine, yielding the *o*-toluidide,  $\text{CH}_3\cdot[\text{CH}]_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , colourless crystals, m. p. 173°.

*Sorbyl cyanide* is obtained by treating an ethereal solution of sorbyl chloride with hydrogen cyanide and pyridine; it is a yellow oil with a pleasant odour. W. H. G.

**Action of Hydroxylamine on Coumarins.** THEODOR POSNER (*Ber.*, 1909, 42, 2523—2532).—A claim of priority over Francesconi and Cusmano (this vol., i, 233). The compound described as dihydroxylaminohydrocoumarin by these investigators is a mixture. Free hydroxylamine and coumarin in cold methyl-alcoholic solution react with rupture of the lactone ring, yielding unstable *β-hydroxylaminodihydrocoumarohydroxamoxime hydroxide*,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{C}(\text{NH}\cdot\text{OH})_2\cdot\text{OH}$ , a white, crystalline powder, which decomposes at 123°, regenerates coumarin when heated with hydrochloric acid, and yields *β*-aminodihydrocoumaric acid, m. p. 214° (208°: Francesconi and Cusmano), when treated with warm solvents. The same acid is obtained by heating coumaric acid or its acetyl derivative with an excess of alcoholic hydroxylamine, although in these two cases the steric influence of the ortho OH-group retards the reactions. *Diacetyl-β-aminodihydrocoumarin*,  $\text{NaAc}_2\cdot\text{CH}\begin{matrix} \text{C}_6\text{H}_4\cdot\text{O} \\ \diagup \\ \text{CH}_2-\text{CO} \end{matrix}$ , m. p. 116—117°, obtained from *β*-aminodihydrocoumaric acid and acetic anhydride, is insoluble in sodium carbonate, whilst *benzoyl-β-aminodihydrocoumaric acid*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NHBz})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 168—169°, is readily soluble in this alkali carbonate. These facts and also the exactly analogous behaviour of *β*-aminodihydrocoumaric acid to that of *β*-aminodihydrocinnamic acid (*Abstr.*, 1906, i, 955; 1907, i, 212) are in favour of the constitution  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , as against the cyclic formula advocated by Francesconi and Cusmano for *β*-aminodihydrocoumaric acid. C. S.

**Some Amino- and Nitroamino-derivatives of Benzoic, *m*-Toluic, and *iso*Phthalic Acids.** MARSTON T. BOGERT and ALFRED H. KROFF (*J. Amer. Chem. Soc.*, 1909, 31, 841—848).—In earlier papers (Bogert and Dox, *Abstr.*, 1905, i, 841, 949; Bogert and

Nelson, Abstr., 1907 i, 660), several derivatives of 2:5-diamino-terephthalic acid have been described. The present work deals chiefly with 4:6-diaminoisophthalic acid and its derivatives.

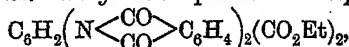
Errera and Maltese (Abstr., 1904, i, 307) attempted to prepare 4:6-diaminoisophthalic acid, but without success, and on repeating their experiments, the present authors also failed to obtain it. The acid has been prepared, however, by converting diacetyl-amino-*m*-xylene into 4:6-diacetyl-aminoisophthalic acid by oxidation with potassium permanganate and boiling this compound with strong hydrochloric acid.

Diacetyl-amino-*m*-xylene melts at  $295.2^{\circ}$  (corr.). 4:6-Diacetyl-aminoisophthalic acid,  $C_6H_2(NHAc)_2(CO_2H)_2$ , m. p.  $276.2^{\circ}$  (decomp., corr.), forms long, colourless needles; its *methyl* and *ethyl* esters melt at  $256^{\circ}$  (corr.) and  $230.4^{\circ}$  (corr.) respectively. 4:6-Diaminoisophthalic acid,  $C_6H_2(NH_2)_2(CO_2H)_2$ , m. p.  $235^{\circ}$  (corr.), is obtained as a pink powder, and dissolves in alkali hydroxide to form a fluorescent solution; its *hydrochloride* melts at  $229-230^{\circ}$  (corr.). The *diethyl* ester, m. p.  $171.5^{\circ}$  (corr.), crystallises in long, yellow needles; its *hydrochloride* melts at  $245.4^{\circ}$  (corr.). The *monoethyl* ester, m. p.  $211.6^{\circ}$  (corr.), forms reddish-yellow prisms. The *dimethyl* ester, m. p.  $204.6^{\circ}$  (corr.), crystallises in red needles; its *hydrochloride* melts at  $235.5^{\circ}$  (decomp.).

The *dilactam* of 4:6-diacetyl-aminoisophthalic acid (*m-bisacetanthranil*),  $\begin{matrix} NAc \\ CO \end{matrix} > C_6H_4 < \begin{matrix} NAc \\ CO \end{matrix}$ , m. p.  $282.3^{\circ}$  (corr.), forms colourless needles; it generally condenses with ammonia and primary amines to produce 1:3:7:9-naphthetetrazines, but with *isoamylamine* it yields the intermediate 4:6-diacetyl-aminoisophthalisoamylamide,

$C_6H_2(NHAc)_2(CO \cdot NH \cdot C_5H_{11})_2$ , m. p.  $189.6^{\circ}$  (corr.), which crystallises in long, silky needles, and can also be obtained by the action of *isoamylamine* on ethyl 4:6-diacetyl-aminoisophthalate.

4:6-Diformylaminoisophthalic acid,  $C_6H_2(NH \cdot CHO)_2(CO_2H)_2$ , m. p. above  $360^{\circ}$ , forms minute needles. *Ethyl* 4:6-diphenylcarbaminoisophthalate,  $C_6H_2(NH \cdot CO \cdot NHPh)_2(CO_2Et)_2$ , m. p.  $256.8^{\circ}$  (corr.), obtained by heating ethyl 4:6-diaminoisophthalate with phenylcarbamide, crystallises in needles. *Ethyl* 4:6-diphthaliminoisophthalate,



m. p.  $251.8^{\circ}$  (corr.), obtained by fusing ethyl 4:6-diaminoisophthalate with phthalic anhydride, forms cream-coloured crystals.

4:6-Diacetyl-amino-*m*-toluic acid,  $O_6H_2Me(NHAc)_2 \cdot CO_2H$ , m. p.  $272.4^{\circ}$  (corr.), obtained as a by-product in the oxidation of diacetyl-amino-*m*-xylene, crystallises in colourless needles, and when boiled with acetic anhydride is converted into 4-acetyl-amino-5-methylacetyl-

*anthranil*,  $NHAc \cdot C_6H_2Me \begin{matrix} CO \\ NAc \end{matrix}$ , m. p.  $166.2^{\circ}$  (corr.). 4-Nitroacetyl-

*anthranil-5-carboxylic acid*,  $CO_2H \cdot C_6H_2(NO_2) \begin{matrix} CO \\ NAc \end{matrix}$ , m. p.  $274.4^{\circ}$  (corr.), obtained by boiling 6-nitro-4-aminoisophthalic acid (Errera and Maltese, *loc. cit.*) with acetic anhydride, forms yellow crystals.

When 6-nitro-4-aminoisophthalic acid is heated with 50% sulphuric acid, it loses carbon dioxide and yields a mixture of 2-nitro-4-amino- and 4-nitro-2-amino-benzoic acids. 2-Nitro-4-acetotoluidide melts at  $148.5^{\circ}$  (corr.), and on oxidation with potassium permanganate yields 2-nitro-4-acetylaminobenzoic acid, m. p.  $219^{\circ}$  (corr.). The latter compound, on hydrolysis, is converted into 2-nitro-4-aminobenzoic acid, m. p.  $239.5^{\circ}$  (corr.), which has recently been prepared by Lucius and Brüning (D.R.-P. 204884) by the partial reduction of 2:4-dinitrobenzoic acid.

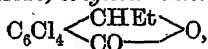
The mother liquors obtained in the preparation of ethyl 4:6-diaminoisophthalate yielded a dark red substance, m. p. about  $102^{\circ}$ , which, when boiled with acetic anhydride, furnished a compound, m. p.  $189.4^{\circ}$  (corr.), which was probably ethyl 2:4-diacetylaminobenzoate.

E. G.

**Action of Organo-magnesium Compounds on Anhydrides of Dicarboxylic Acids.** HUGO BAUER (*Arch. Pharm.*, 1909, 247, 220—225).—The author has shown previously (Abstr., 1904, i, 417; 1905, i, 210) that the normal reaction between magnesium alkyl haloids and phthalic anhydride results in the formation of dialkyl-phthalides. Houben and Hahn have observed, however, that in the case of camphoric anhydride some monoalkylcampholide is also formed, and have also noted other variations of the normal reaction (Abstr., 1908, i, 539). The author has therefore examined several other condensations of this type.

Propyl chloride reacts with magnesium powder and phthalic anhydride to form *dipropylphthalide*,  $C_6H_4 \begin{smallmatrix} \text{CPr}^a \\ \text{CO} \end{smallmatrix} O$ , m. p.  $76^{\circ}$ , which crystallises in flat prisms and is readily soluble in most organic solvents. *Diisopropylphthalide*, m. p.  $83-84^{\circ}$ , similarly obtained, forms long crystals, and is easily soluble in hot alcohol and difficultly so in cold alcohol.

Magnesium methyl iodide reacts with tetrachlorophthalic anhydride to form *dimethyltetrachlorophthalide*, m. p.  $165-166^{\circ}$ , which crystallises in slender, colourless needles. With magnesium ethyl bromide and tetrachlorophthalic anhydride, *ethyltetrachlorophthalide*,

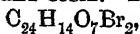


m. p.  $132-133^{\circ}$ , is formed. It crystallises from alcohol in almost colourless needles, and is remarkably stable towards nitric acid, being precipitated unchanged from solution in the acid by water. With magnesium *p*-tolyl bromide, phthalic anhydride reacts to form *o*-di-*p*-toluoylbenzene,  $C_6H_4(CO \cdot C_6H_4Me)_2$ , m. p.  $190-191^{\circ}$ , which crystallises from alcohol. Magnesium phenyl bromide gives with tetrachlorophthalic anhydride a mixture of mono- and di-phenyltetrachlorophthalides, which it has so far proved impossible to separate into its components.

T. A. H.

**Asymmetric Dibromofluorescein.** GUSTAV HELLER and HEINRICH L. MEYER (*Ber.*, 1909, 42, 2188—2190).—Baeyer's *as*-dibromofluorescein (this Journ., 1877, i, 200) is best prepared by heating a mixture of dibromodihydroxybenzoic acid and resorcinol in

molecular proportions with zinc chloride (20%) at  $170^{\circ}$  for two hours. It crystallises from alcohol in dark red prisms,  $C_{20}H_{10}O_5Br_2 \cdot C_2H_6O$ , m. p. about  $300^{\circ}$ . The fluorescence of its alkaline solutions is midway between those of fluorescein and eosin. The *diacetyl* derivative,



crystallises from toluene in colourless, flat plates containing a molecule of toluene, m. p.  $173^{\circ}$  (decomp.). When heated with 50% sodium hydroxide solution at  $130$ — $135^{\circ}$ , the dibromofluorescein yields dibromodihydroxybenzoylbenzoic acid, but not dihydroxybenzoylbenzoic acid.

J. J. S.

**Cholic Acids.** MAURICE PIETTRE (*Compt. rend.*, 1909, 148, 1779—1782).—It is shown that the cholic acids of bile differ between themselves, and not only in the fact that they exist in combination with different amino-acids. Cholic acid, prepared by the hydrolysis of pure sodium glycocholate (Abstr., 1908, i, 959), is a yellow, resinous mass, which, on distillation under ordinary pressure, loses water and forms a pitch-like mass having the properties of an acid, and agreeing with the formula  $C_{25}H_{43}O_3$ . The acid obtained on hydrolysing sodium taurocholate differs from the foregoing in that it cannot be distilled, and undergoes reduction by sodium and amyl alcohol, giving a colourless, tasteless, crystalline compound,  $C_{24}H_{42}O_5$ , m. p.  $180^{\circ}$ ,  $[\alpha]_D + 54^{\circ}46'$ .

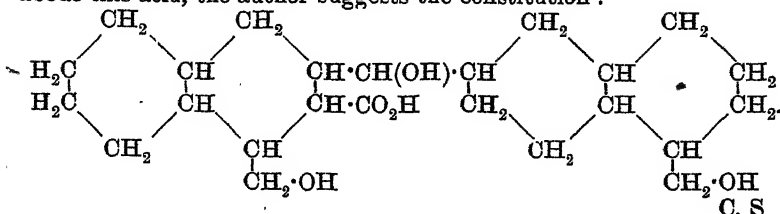
W. O. W.

**Energetic Oxidation of Cholic Acid by Nitric Acid.** THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1909, 60, 376—407).—Cholecamphoric (choloidanic) acid, obtained by oxidising cholic acid by concentrated nitric acid, is destroyed by the prolonged action of the mineral acid. To examine the complex mixture of oxidation products, the following process is used. Cholic acid, freed from fatty acids, is heated with nitric acid, D 1.4, for three days, repeatedly evaporated with water to remove nitrous acid, dissolved in hot water, and the cold solution treated with lead acetate, whereby a voluminous precipitate is obtained. The filtrate contains succinic acid, a glutaric acid,  $\alpha$ -methylglutaric acid, and a saturated, dibasic acid,  $C_8H_{12}O_5$ , which is probably 1-hydroxycyclohexane-1:4-dicarboxylic acid, since *p*-hydroxybenzaldehyde has been prepared from it.

From the lead acetate precipitate an individual, crystalline substance has not been isolated, but, after removal of the lead, a number of fractions, all oils of acid character, has been obtained by the use of different solvents and precipitants. Of these fractions, the following appear to be individual substances: a saturated, dibasic acid,  $C_8H_{14}O_5$ , which is oxidised by hydrogen peroxide to a saturated, dibasic acid,  $C_8H_{12}O_5$ ; an unsaturated acid, oxidised by hydrogen peroxide to a saturated, tribasic acid,  $C_{12}H_{18}O_6$ ; and a saturated, dibasic acid,  $C_8H_{12}O_5$ , which is oxidised by hydrogen peroxide to an unsaturated, monobasic acid,  $C_7H_{10}O_4$ , possibly a dihydroxycyclohexenecarboxylic acid.

The chief result of the investigation is the probability that cholic

acid is a derivative of *cyclohexane*; taking into account the facts known about this acid, the author suggests the constitution:



**Glycocholic and Para-glycocholic Acids.** E. LETSCHE (*Zeitsch. physikal. Chem.*, 1909, 60, 462—475).—Glycocholic acid was obtained from ox-bile by Hüfner's method. Para-glycocholic acid arises from it at a high temperature or in the absence of water; in the presence of water the reaction is reversible. The two acids differ in some of their constants; they are physical isomerides.

The melting point of glycocholic acid depends on the method of heating.

Glycocholic acid has  $[\alpha]_D + 32.3^\circ$ ; the sodium salt has  $[\alpha]_D + 24.3^\circ$  in water, and  $+ 27.8^\circ$  in 90% alcohol. Hoppe-Seyler's figures are too low.

W. D. H.

**Elateric Acid.** ARMAND BERG (*Compt. rend.*, 1909, 148, 1679—1681. Compare Abstr., 1898, ii, 407; 1906, i, 596; 1907, i, 146; this vol., i, 248).—Further details are given of the preparation of elateric acid from elateridin, and of the solubility of the acid and its salts.

Elateric acid,  $C_{28}H_{38}O_7$ , has m. p.  $73-75^\circ$ ; all its salts are amorphous. The author does not agree with Hemmelmayr's view (Abstr., 1907, i, 230), that elateric acid is formed by the oxidation of a CHO-group in elateridin, since it can be obtained by treating this substance with alcoholic sodium hydroxide in the absence of free oxygen.

W. O. W.

**Artificial Preparation and Constitution of Ellagic Acid.** PAUL SISLEY (*Bull. Soc. chim.*, 1909, [iv], 5, 727—730).—Ellagic acid was first prepared artificially by Zwenger and Ernst (*Annalen*, 1871, 159, 27), whose results were confirmed by Herzig and Pollak (Abstr., 1908, i, 546). The author has described previously (*Ann. Soc. Agric. Sci. Ind. Lyon*, 1895, 34) a method of preparation depending on the aerial oxidation of tannin in alkaline solution. Pure tannin (1 mol.), prepared from China galls (Abstr., 1894, ii, 169), is dissolved in alcohol ( $40^\circ$ ), treated with an aqueous solution ( $40^\circ$  Baumé) of potassium hydroxide (2 mols.), and the mixture exposed to the air in photographic dishes, when potassium hydrogen ellagate is deposited. In this way a 50% yield is obtained compared with the 35% resulting in the Zwenger and Ernst process. Ellagic acid crystallises with  $2H_2O$ , which is lost at  $130^\circ$ , but the anhydrous acid re-absorbs the water very rapidly when exposed to the air. This method of formation

confirms the constitution of ellagic acid proposed by Graebe (Abstr., 1903, i, 262) and supported by Perkin and Nierenstein (Trans., 1906, 87, 1412), and also that of gallotannic acid, from which it is obtained by oxidation. The author agrees with Nierenstein (this vol., i, 174) that gallotannic acid is not a glucoside, and shows by converting it into gallic acid that it is a digallic acid. E. H.

**Distribution of Chlorogenic Acid in Nature.** K. GORTER (*Arch. Pharm.*, 1909, 247, 184—196).—The paper is prefaced by a short description of the chief properties and characters of the acid as already published (Abstr., 1908, i, 186, 345). For the detection of the acid in plants, the following colour reaction is used. Ten grams of leaves are boiled with 50 c.c. of dilute hydrochloric acid during one hour in a reflux apparatus. The filtrate from this is shaken with 15 c.c. of ether. The latter is washed with a dilute solution of sodium hydrogen carbonate and then twice with water, and to it is added a small quantity of a very dilute solution of ferric chloride, when, if chlorogenic acid is present in the leaves, a violet coloration is produced in the aqueous layer on shaking, whilst the ethereal layer develops a yellow tint. Out of 230 species of plants examined in this way, 98 gave a positive result. The acid appears to occur in many plants of the orders: *Araliaceae*, *Convolvulaceae*, *Boraginaceae*, *Gesneraceae*, *Acanthaceae*, and *Compositae*. T. A. H.

**Igasuric Acid.** K. GORTER (*Arch. Pharm.*, 1909, 247, 197—200).—This name was first given by Pelletier and Caventou to a crystalline acid isolated from nux-vomica seeds. Later investigators have always obtained it in an amorphous state, and Sander (Abstr., 1897, i, 383) regarded it as identical with caffetannic acid. The author finds that it is identical with the chlorogenic acid obtained by him from coffee berries (Abstr., 1908, i, 186, 345, and preceding abstract). Pelletier and Caventou's acid, he suggests, may have been impure quinic acid, since the latter is produced by the action of alkalis on chlorogenic acid. T. A. H.

**Action of Ammonia on Benzaldehyde and the Preparation of Benzaldehyde-ammonia.** FRANCIS FRANCIS (*Ber.*, 1909, 42, 2216—2218).—Hydrobenzamide is most readily prepared by shaking a concentrated solution of ammonia with an emulsion of benzaldehyde containing a little soap solution.

*Benzaldehyde-ammonia*,  $2C_6H_5 \cdot CHO \cdot NH_2$ , probably  $NH(CHPh \cdot OH)_2$ ,

is readily obtained by adding concentrated aqueous ammonia and alcohol to a mixture of benzaldehyde and a little alcohol at  $0^\circ$  and then cooling to  $-20^\circ$ , when the additive compound separates in the form of well developed plates, m. p.  $45^\circ$ . The formation of the compound is favoured by the presence of alkalis, whereas ammonium chloride tends to produce hydrobenzamide. When kept for some time, the additive compound yields hydrobenzamide, benzaldehyde, and water. With benzoyl chloride and potassium carbonate, it yields

a small amount of benzylidenedibenzamide (Hoffmann and V. Meyer, *Abstr.*, 1892, 604).

The additive compound is undoubtedly an intermediate product in the preparation of hydrobenzamide. *p-Tolualdehyde-ammonia*,  $2\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}\cdot\text{NH}_3$ , melts at  $43-44^\circ$ , and is less stable than the benzaldehyde compound. It readily yields *p-trimethylhydrobenzamide*,  $(\text{C}_6\text{H}_4\text{Me}\cdot\text{CH})_3\text{N}_2$ , m. p.  $95^\circ$ .

An additive compound could not be obtained from anisaldehyde and ammonia.

J. J. S.

***o*-Nitrosobenzaldehyde.** EUGEN BAMBERGER and ANDOR FODOR (*Ber.*, 1909, 42, 2573—2574. Compare this vol., i, 509).—*o-Nitrosobenzaldehyde* is obtained by the decomposition of *o*-aldehydonitrosophenylhydroxylamine with acids as white, glistening needles, m. p.  $109-110^\circ$ .

[With O. BAUDISCH].—Zinc dust and amyl nitrite convert *o*-nitrobenzaldehyde into *o*-aldehydonitrosophenylhydroxylamine.

C. H. D.

**Optically Active Benzaldehydecyanohydrin.** KARL FEIST (*Arch. Pharm.*, 1909, 247, 226—232. Compare *Abstr.*, 1908, i, 437, 903; Rosenthaler, *ibid.*, i, 817; Auld, *Trans.*, 1909, 95, 927).—Since Rosenthaler has shown that *d*-benzaldehydecyanohydrin is formed by the action of emulsin on a mixture of benzaldehyde and hydrocyanic acid, it ought to be possible to prepare *l*-benzaldehydecyanohydrin by the action of emulsin on *dl*-benzaldehydecyanohydrin, since it is also known that only the *d*-form is destroyed by the enzyme. This proves to be the case, and a slightly *laevo*-product can be obtained by allowing emulsin to react with the *dl*-form in presence of much water and a little alcohol during forty-eight hours, the hydrogen cyanide formed being carried away by a stream of air passed through the mixture. This *l*-product, on hydrolysis, yields *d*-mandelic acid.

Further evidence is brought forward in favour of the view that *d*-benzaldehydecyanohydrin ( $[\alpha]_D = 14^\circ$ ) is the first product of the action of emulsin on amygdalin (*loc. cit.*), and it is shown that auto-racemisation of the *d*-form does not occur at ordinary temperatures, but that, in presence of water, racemisation occurs slowly, although no hydrogen cyanide is split off.

T. A. H.

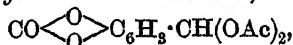
**A Synthesis of Aldehydes and Indole. III.** R. A. WEERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 42—44. Compare *Abstr.*, 1908, i, 22).—Methyl styrylcarbamate on hydrolysis with acid yields phenylacetaldehyde, the *oxime*,  $\text{C}_8\text{H}_9\text{ON}$ , of which has m. p.  $99-100^\circ$ .

*o*-Nitrophenylacetaldehyde,  $\text{C}_8\text{H}_7\text{O}_2\text{N}$ , obtained similarly from methyl *o*-nitrostyrylcarbamate, has b. p.  $133-135^\circ/5\text{ mm.}$ , m. p.  $22-23^\circ$ ; its alkaline solution turns red. The *oxime*,  $\text{C}_8\text{H}_9\text{O}_2\text{N}_2$ , crystallises from water in long needles, m. p.  $110^\circ$ . The *m*- and *p*-nitrophenylacetaldehydes can also be obtained from the corresponding carbamates. It is thus rendered possible to synthesise an aldehyde containing one carbon atom less from a cinnamide.

Indole is obtained when *o*-nitrophenylacetaldehyde is reduced with iron in hydrogen sulphite solution, or, better, by the reduction of the methyl *o*-nitrostyrylcarbamate.

W. R.

"Dichloropiperonal." HERMANN PAULY and THOMAS J. R. ALEXANDER (*Ber.*, 1909, 42, 2350—2354. Compare Abstr., 1907, i, 709; this vol., i, 165).—"Dichloropiperonal," the structure of which is established as the carbonate of 3:4-dihydroxybenzylidene chloride, cannot be hydrolysed to the corresponding phenol; instead, protocatechualdehyde is formed. When the theoretical quantity of water and dry pyridine are used to effect hydrolysis, an orange-brown chloro-compound was obtained; using methyl alcohol and pyridine, or, better, sodium acetate, *methylprotocatechualdehyde-m-carbonate* is obtained; this is a syrup solidifying to minute needles, m. p. 93°. On boiling dichloropiperonal with sodium acetate and acetic anhydride, *dihydroxybenzylideneglycol carbonate diacetate*,



is formed, m. p. 84.5—85°. By the partial reduction of dichloropiperonal in absolutely anhydrous acetic acid with zinc dust, the carbonate of *dihydroxybenzyl chloride*,  $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH}_2\text{Cl}$ , is obtained; this crystallises in very long, lustrous needles, m. p. 53.5—54°, and interacts with silver acetate, forming the carbonate acetate of 3:4-dihydroxybenzyl alcohol,  $\text{CO} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{OAc}$ , separating in microscopic needles, m. p. 59.5°. The monochloride is hydrolysed by the theoretical quantity of water in presence of pyridine, but the product immediately combines with pyridine to form 3:4-dihydroxybenzylpyridinium chloride,  $\text{C}_6\text{H}_3(\text{OH})_2 \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_5\text{Cl}$ , crystallising in prismatic plates, m. p. 170—171° (corr.).

E. F. A.

Preparation of Hydroxyuvitaldehyde from *p*-Cresol. FRITZ ULLMANN and KARL BRITTENER (*Ber.*, 1909, 42, 2539—2548).—*p*-Cresol, 35% formaldehyde, and concentrated sodium hydroxide react in four days to form the sodium salt of 3:5-dimethylol-*p*-cresol (Auwers, Abstr., 1907, i, 610). The alcohol, liberated by acetic acid, yields 3:5-dinitro-*p*-cresol by treatment with 30% nitric acid, and is converted by alkali and methyl sulphate into *methoxyuvital alcohol*,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}(\text{CH}_2 \cdot \text{OH})_2$  [= 4:1:3:5], m. p. 106.5° (corr.), which is oxidised by cold alkaline potassium permanganate to 4-methoxyuvitic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}(\text{CO}_2\text{H})_2$ , m. p. 180° (corr.), which, by gentle warming with hydriodic acid, D 1.7, is converted into hydroxyuvitic acid. Methoxyuvitic acid is oxidised by hot potassium permanganate to *methoxytrimesic acid*,  $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{CO}_2\text{H})_3$ , m. p. 248°, which yields anisole above its m. p., forms a trimethyl ester, m. p. 86° (corr.), with methyl sulphate and sodium carbonate, and is converted by hydriodic acid into hydroxytrimesic acid.

Methoxyuvityl alcohol is oxidised by sodium dichromate and hot dilute sulphuric acid to *methoxyuvitaldehyde*,  $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Me}(\text{CHO})_2$ , m. p.  $96^\circ$  (corr.), which forms a *bisphenylhydrazone*, m. p.  $185\cdot5^\circ$  (decomp.), and a *dioxime*, m. p.  $193^\circ$  (corr.). The conversion of the methoxy-derivative into 4-hydroxyuvitaldehyde can be effected by heating with aluminium chloride in benzene, but the aldehyde is more readily obtained as follows. By shaking a mixture of aqueous 3 : 5-dimethylol-*p*-cresol and sodium hydroxide with toluenesulphonyl chloride in benzene, the *ester*,  $\text{C}_6\text{H}_2\text{Me}(\text{CH}_2\cdot\text{OH})_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ , m. p.  $132\cdot5^\circ$  (corr.), is obtained, which is oxidised by sodium dichromate and glacial acetic acid to the *compound*,  $\text{C}_6\text{H}_2\text{Me}(\text{CHO})_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ , m. p.  $146\cdot5^\circ$ , which is quantitatively hydrolysed by concentrated sulphuric acid, yielding *4-hydroxyuvitaldehyde*,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}(\text{CHO})_2$ , m. p.  $133\cdot5^\circ$ , which begins to sublime at  $100^\circ$ , gives a yellowish-green, fluorescent solution in water (due to alkali in the glass vessel), and forms a *bisphenylhydrazone*, m. p.  $185^\circ$  (decomp.), and a *dioxime*, m. p.  $199^\circ$  (corr.).

Methoxyuvitaldehyde condenses with dimethylaniline in the presence of zinc chloride to form a colourless leuco-compound, which oxidises to a green dye, *4-methoxy-1-methyl-3 : 5-bistetramethyldiaminobenzhydrylbenzene*,  $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Me}[\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2]_2$ , m. p.  $252^\circ$ .

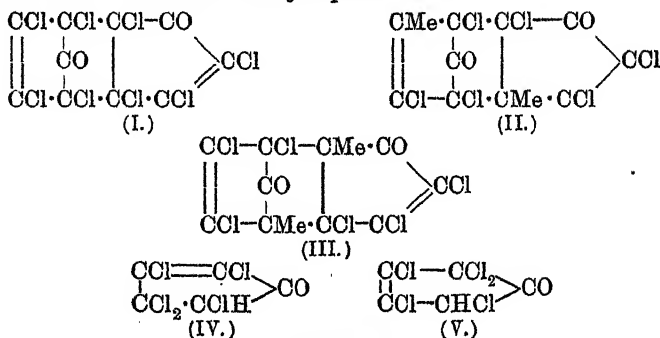
C. S.

**Transformation of *cyclopentene* Derivatives into Indene Derivatives.** THEODOR ZINCKE and KURT H. MEYER (*Annalen*, 1909, 367, 1—13).—It has been shown by Zincke and Küster (Abstr., 1890, 1255) that hexachloro-1-hydroxy- $\Delta^2$ -*cyclopentene*-1-carboxylic acid and the corresponding  $\Delta^2$ -*cyclopentene* compound when boiled with water yield hexachloroindone. On the other hand, derivatives of these acids containing one or two chlorine atoms replaced by methyl, when similarly treated, do not yield indene derivatives, but substances having the formulæ  $\text{C}_{10}\text{Me}_2\text{O}_2\text{Cl}_6$  and  $\text{C}_{10}\text{Me}_4\text{O}_2\text{Cl}_4$  (compare Zincke, Bergmann, and Franke, Abstr., 1897, i, 507; Zincke and Prenzel, Abstr., 1897, i, 509). This subject has been re-investigated, and a substance,  $\text{C}_{10}\text{O}_2\text{Cl}_8$ , obtained as an intermediate product in the conversion of hexachlorohydroxycyclopentenecarboxylic acid, m. p.  $186^\circ$ , into hexachloroindone. The isomeric acid, m. p.  $111^\circ$ , is decomposed so slowly by water that the substance  $\text{C}_{10}\text{O}_2\text{Cl}_8$  could not be isolated; it is probable, however, that the acid at first decomposes, thus:  $\text{C}_6\text{H}_2\text{O}_2\text{Cl}_6 = \text{C}_5\text{HOCl}_5 + \text{CO}_2 + \text{HCl}$ ; the substance  $\text{C}_5\text{HOCl}_5$  has not been obtained in this manner, but by the reduction of the hexachlorocyclopentenone, m. p.  $28^\circ$ ; it passes into the substance  $\text{C}_{10}\text{O}_2\text{Cl}_8$  with elimination of hydrogen chloride. The substance  $\text{C}_{10}\text{O}_2\text{Cl}_8$  probably has the constitution (I), whilst the homologues may be represented by (II) and (III).

The stability of the homologues is undoubtedly due to the presence of the methyl groups in place of the labile chlorine atoms.

The substance  $\text{C}_5\text{HOCl}_5$  has the formula (IV) or (V), since it does not form an acetyl derivative with acetic anhydride, and yields with

phosphorus pentachloride a substance  $C_5Cl_8$ , which may also be prepared from the hexachlorocyclopentenones.



*Pentachlorocyclopentenone*,  $\begin{array}{c} \text{CCl} = \text{CCl} \\ | \quad | \\ \text{CCl}_2 \cdot \text{CHCl} \end{array} > \text{CO}$ , prepared by the action of stannous chloride in glacial acetic acid on hexachlorocyclopentenone, m. p.  $28^\circ$ , crystallises in colourless needles, m. p.  $81-82^\circ$ . When warmed with glacial acetic acid and sodium acetate, it is converted into the substance  $C_{10}O_2Cl_8$ , which has already been described (Zincke, Abstr., 1897, i, 507).

*Decachlorohydrindene*,  $C_{10}Cl_8 < \begin{array}{c} \text{CCl}_2 \\ | \\ \text{CCl}_2 \end{array} > \text{CCl}_2$ , is prepared by heating the substance  $C_{10}O_2Cl_8$  with phosphorus pentachloride under pressure at  $280^\circ$ ; it crystallises in small, glistening prisms, m. p.  $135^\circ$ .

*Pentachloroaminoindone*,  $C_8Cl_4 < \begin{array}{c} \text{CO} \\ | \\ \text{C}(\text{NH}_2) \end{array} > \text{CCl}$ , is formed by the action of ammonia on the substance  $C_{10}O_2Cl_8$ , or pentachlorocyclopentenone; it crystallises in orange needles, m. p.  $205^\circ$ . W. H. G.

**Dichlorocyclohexenones and cycloHexadienes from o-Cresol.** KARL AUWERS and FRIEDRICH VON DER HEYDEN (*Ber.*, 1909, 42, 2404—2423. Compare Abstr., 1908, i, 550—551).—A number of hydroaromatic ketones and hydrocarbons were synthesised with the object of determining the effect of the position of the double linking on the optical and other physical properties of cyclic compounds, and it is found that in the case of the ketones the shifting of a double linking into the conjugated position to the double linking of the carbonyl group produces an exaltation of molecular refraction and dispersion as well as a rise in boiling point and density; similarly, in the case of the hydrocarbons it is found that conjugated ethylene linkings produce exaltation in optical properties in accordance with Brühl's laws, and the authors are, accordingly, of opinion that a careful determination of the physical constants of compounds of this kind is a more trustworthy criterion of their purity than any chemical reactions, such as oxidation, etc., which are not of a quantitative nature.

1-Methyl-1-dichloromethylcyclohexadienone and the corresponding 4-methyl derivative were prepared as previously described (Abstr.,

1908, i, 550); they have b. p. 115—115.5°/13 mm. and 140—142°/13 mm. respectively.

1-Methyl-1-dichloromethyl-4-ethyl- $\Delta^2$ -cyclohexen-6-one, best prepared by previously activating the magnesium by means of methyl iodide, should have  $D_4^{180}$  1.1671 or  $D_4^{184}$  1.1683, instead of the higher value previously quoted.

1-Methyl-1-dichloromethyl-4-isopropyl- $\Delta^2$ -cyclohexen-6-one,  $C_{11}H_{16}OCl_2$ , obtained in 80—90% yield by the action of magnesium isopropyl iodide on the chloroketone, is a colourless oil, b. p. 135.4—136.4°/8 mm.,  $D_4^{183}$  1.1421,  $n_D^{168}$  1.50142. When poured into ice-cold concentrated sulphuric acid, the double linking is shifted from the 2 to the 3 position and there results.

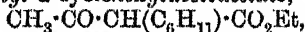
1-Methyl-1-dichloromethyl-4-isopropyl- $\Delta^3$ -cyclohexen-2-one,  $C_{11}H_{16}OCl_2$ , b. p. 149.4—150.4°/7 mm.,  $D_4^{158}$  1.1654,  $n_D^{158}$  1.51769. The following substances were also prepared by a similar shifting of the double bond: 1-methyl-1-dichloromethyl-4-ethyl- $\Delta^3$ -cyclohexen-2-one,  $C_{10}H_{14}OCl_2$ , b. p. 150.8—151.2°/10 mm.,  $D_4^{180}$  1.1953,  $n_D^{177}$  1.52331, and 1:4-dimethyl-1-dichloromethyl- $\Delta^3$ -cyclohexen-2-one, which has been previously described, but for which some new physical data are given.

1-Methyl-4-isopropyl- $\Delta^{1:3}$ -cyclohexadiene or  $\Delta^{1:3}$ -dihydrocymene, obtained by the action of boiling alcoholic potash on the corresponding ketone, appears to be identical with the substance described by Wallach as  $\alpha$ -terpinene, since it behaved like this substance on oxidation, giving rise to  $\alpha$ -dihydroxy- $\alpha$ -methyl- $\delta$ -isopropyladipic acid (compare Abstr., 1908, i, 813).

P. H.

Hexahydropropio-phenone, Hexahydrobenzyl Methyl Ketone, Ethyl cycloHexylacetoacetate, and a Compound,  $C_{10}H_{12}O_4$ , Obtained in the Preparation of the Acetoacetate CARL HELL and OSCAR SCHAAL (*Ber.*, 1909, 42, 2230—2236).—Hexahydropropio-phenone (V. Meyer and Scharvin, Abstr., 1897, i, 613) can be prepared by oxidising cyclohexylethylcarbinol with chromic acid. The semicarbazone,  $C_{10}H_{19}ON_3$ , crystallises from dilute alcohol in plates, m. p. 149—150°. The carbinol,  $C_6H_{11}\cdot CH_2Et\cdot OH$ , obtained from magnesium cyclohexyl iodide and propaldehyde, is an oil with a penetrating odour, and has b. p. 199—201°.

A small yield of ethyl  $\alpha$ -cyclohexylacetouacetate,



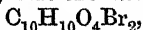
is obtained by the action of cyclohexyl iodide on sodioethylacetoacetate. It is a colourless liquid, b. p. 126—127°/14 mm. The semicarbazone,  $C_{13}H_{23}O_3N$ , crystallises from aqueous acetone in cubes, m. p. 114°. The free acid,  $CH_3\cdot CO\cdot CH(C_6H_{11})\cdot CO_2H$ , has m. p. 67—68°, and decomposes readily into carbon dioxide and hexahydrobenzyl methyl ketone.

Other products obtained in the preparation of ethyl cyclohexylacetoacetate are: cyclohexene, hexahydrobenzyl methyl ketone, ethyl dicyclohexylacetoacetate, and a compound,  $C_{10}H_{12}O_4$ .

Hexahydrobenzyl methyl ketone,  $C_6H_{11}\cdot CH_2\cdot CO\cdot CH_3$ , obtained by the ketonic hydrolysis of the acetoacetate, is a colourless liquid, b. p. 195—196°; its semicarbazone,  $C_{10}H_{19}ON_3$ , has been analysed.

The compound,  $C_{10}H_{12}O_4$ , crystallises from dilute alcohol in long

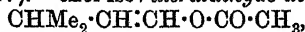
needles, m. p. 61°. It combines with bromine, but at the same time loses hydrogen bromide and yields the *dibromo*-derivative,



which crystallises from light petroleum in prisms, m. p. 118—119°.

J. J. S.

**Components of Ethereal Oils.** *enol-isoValeraldehyde Acetate* and *enol-Citronellal Acetate*, and the Conversion of the Latter into *isoPulegol Acetate*. FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 2014—2017).—*enol-isoValeraldehyde acetate*,



prepared by heating *isovaleraldehyde* with acetic anhydride and sodium acetate in an autoclave, is an oil, b. p. 127—133°,  $D_{20}^{20}$  0.8818,  $n_D^{20}$  1.41655. A small quantity of diacetate is formed at the same time, which decomposes during distillation into monoacetate.

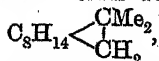
*enol-Citronellal acetate*,  $\text{C}_{10}\text{H}_{17}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ , is an oil, b. p. 110—115°/10 mm.,  $D_{20}^{20}$  0.902,  $n_D^{20}$  1.45762,  $[\alpha]_D^{20}$  -1°. A fraction b. p. 125—150°/10 mm. consisted mainly of diacetate. On boiling the monoacetate with acetic anhydride and acetic acid for twenty hours, *isopulegol acetate*, b. p. 100—105°/10 mm.,  $D_{20}^{20}$  0.925,  $n_D^{20}$  1.459, is formed (compare Tiemann and Schmidt, *Abstr.*, 1897, i, 198).

E. F. A.

[Combinations of Camphor with Phenols.] E. CAILLE (*Compt. rend.*, 1909, 148, 1458—1461).—The author has examined the freezing-point curves of mixtures of  $\beta$ -bromocamphor with salol (phenyl salicylate) and of camphor with salol,  $\alpha$ - and  $\beta$ -naphthols, and resorcinol. In each case the curves show minima corresponding with the existence of eutectic mixtures. No evidence has been obtained of the existence of definite compounds, such as have been described by L  ger (*Abstr.*, 1890, 1427). The formation of a compound containing resorcinol and camphor in molecular proportions is indicated, however, by a maximum in the curve.

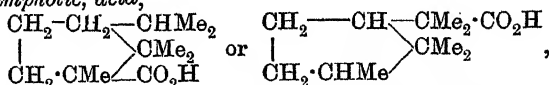
W. O. W.

**Dimethylcamphor and Dimethylcampholic Acid.** ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 148, 1643—1648).—When camphor is treated successively with sodamide and a magnesium alkyl halide, a mixture of mono- and di-alkylcamphors results. The separation of these compounds is affected by treatment with hydroxylamine zinc hydrochloride, when the mono-alkyl derivative alone undergoes oximation. *Dimethylcamphor*,  $\text{C}_8\text{H}_{14}\begin{smallmatrix} \diagup \text{CMe}_2 \\ \diagdown \text{CO} \end{smallmatrix}$ , is a mobile liquid with a camphoraceous odour, b. p. 106°/11 mm.,  $D_4^{20}$  0.94708,  $M_D$  53.21,  $[\alpha]_D^{24}$  92.7°. It does not form a semicarbazone. When reduced by sodium and alcohol it forms *dimethylborneol*,



a crystalline mass, m. p. 18—20° (probably consisting of a mixture of isomerides, since crystals were obtained with m. p. 28—30°), b. p. 109—111°/13 mm.,  $[\alpha]_D^{23}$  32.4°. The *phenylurethane* occurs as needles, m. p.

111.5—112°,  $[\alpha]_D$  29.5°. Dimethylcamphor resembles fenchone (Semmler, Abstr., 1906, i, 681) and the trialkylacetophenones already studied (this vol., i, 131) in its behaviour with sodamide, this reagent converting it into *dimethylcampholamide*,  $C_{12}H_{22}O$ , m. p. 72—73°,  $[\alpha]_D$  70.8°. Sulphuric acid and sodium nitrite convert this into *dimethylcampholic acid*,



m. p. 73—74°,  $[\alpha]_D$  +47.4°. A substance corresponding with the first formula should give camphoric acid on oxidation. The acid actually obtained, however, by oxidising dimethylcampholic acid with potassium permanganate loses carbon dioxide when heated, and has not yet been identified.

W. O. W.

Preparation of *o*-, *m*-, and *p*-Hydroxy-, *p*-Dimethylamino-, and *p*-Diethylamino-benzylidenecamphors, and of *p*- and *m*-Tolylidenecamphors. ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 148, 1490—1496. Compare Abstr., 1891, 1498).—New derivatives of benzylidenecamphor have been prepared with the object of examining the influence of substituents in the benzene ring on the rotatory power of the compounds. The hydroxy-derivatives were obtained by acting on sodium camphor with the acetyl derivatives of *o*-, *m*-, and *p*-hydroxybenzaldehyde; the oily product was then hydrolysed to remove the acetyl group.

*Salicylidenecamphor*,  $C_8H_{14}$   $\begin{array}{c} \text{C}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH} \\ \text{CO} \end{array}$ , occurs as highly refractive crystals, m. p. 209—210°,  $[\alpha]_D$  469°. *m*-Hydroxybenzylidenecamphor has m. p. 144—145°,  $[\alpha]_D$  423°, whilst the *p*-hydroxy-derivative has m. p. 207°,  $[\alpha]_D$  500°. These compounds are colourless, but dissolve in aqueous alkalis, giving yellow solutions which show considerably higher rotatory power.

*p*-Dimethylaminobenzylidenecamphor,  $C_{10}H_{14}O\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , prepared by the general method, forms lamellae, m. p. 139°,  $[\alpha]_D$  758°; the *p*-diethyl derivative,  $C_{19}H_{25}ON$ , forms tablets, m. p. 78—79°,  $[\alpha]_D$  740°, and like the dimethyl compound is yellow, but dissolves in hydrochloric acid, forming a colourless *hydrochloride* readily dissociated by water. The rotatory power of these two bases is considerably lower in acid solutions.

*p*-Tolylidenecamphor,  $C_{10}H_{14}O\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in colourless needles or prisms, m. p. 98°,  $[\alpha]_D$  458°; it combines with hydrogen bromide. The *meta*-derivative forms colourless prisms, m. p. 77.5°,  $[\alpha]_D$  396°. The above specific rotations are those of the compounds in *N*/30-alcoholic solution.

W. O. W.

Synthesis of Derivatives of Racemic Fenchone LOUIS BOUVEAULT and LEVALLOIS (*Compt. rend.*, 1909, 148, 1524—1526. Compare this vol., i, 497).—The following observations render it probable that the low m. p. of synthetic *r*-dihydrofencholenamide is due to the presence of a geometrical isomeride. Hypobromites act on the racemic amide (prepared from the two active amides), giving two

isomeric *carbamides*, m. p. 175° and 161°. The synthetic amide gives two *carbamides*, m. p. 162—163° and 136°. Each active amide forms a carbamide, m. p. 168° (Abstr., 1908, i, 193).

The *r-carbamide*, prepared by mixing the two active forms, has m. p. 185° (175° after re-solidification). After heating for an hour at 200°, however, it can be separated into two isomeric carbamides, m. p. 162—163° and 148°.

The two products having m. p. 162—163° are identical. It follows, therefore, that the synthetic amide contains an isomeride capable of forming the racemic *diapofenchylcarbamide* when treated with hypobromite. The active amides do not undergo the above transformation when heated. W. O. W.

**Alcohols and Aromatic Hydrocarbons Derived from Fenchone.** J. LEROIDE (*Compt. rend.*, 1909, 148, 1611—1613).—Fenchol forms additive compounds with phenyl- and tolyl-magnesium bromides; these are insoluble in ether and toluene, but on prolonged heating with these solvents are converted into the magnesium derivatives of the corresponding tertiary alcohol, *tert-Phenylfenchol*,  $C_{16}H_{22}O$ , has m. p. 47°, b. p. 166—177°/13 mm.,  $[\alpha]_D^{18}$  45·65° in alcohol. Pyruvic acid converts it into a *compound*, m. p. 151—153°. When treated with anhydrous formic or oxalic acid it forms a *hydrocarbon*,  $C_{16}H_{20}$ , b. p. 157—158°/13—14 mm.,  $D_4^{15}$  0·9795,  $[\alpha]_D^{15} + 0·60°$ ,  $n_D^{15}$  1·5536. When the dehydration is effected by potassium hydrogen sulphate, an isomeric *hydrocarbon* is produced, having m. p. 16—17°, b. p. 139—141°/16 mm.,  $[\alpha]_D^{18} + 22·60°$ ; hydrobromic acid converts this into a *bromo-derivative*, m. p. 115—116°.

*tert-o-Tolylfenchol*,  $C_{17}H_{24}O$ , b. p. 175—177°/14 mm.;  $D_4^{15}$  1·0890,  $[\alpha]_D^{18} + 23·23°$ . *tert-p-Tolylfenchol*, b. p. 180—181°/15 mm.,  $D_4^{15}$  1·0272,  $[\alpha]_D^{18} + 16·30°$ . *tert-Benzylfenchol*,  $C_{17}H_{24}O$ , crystallises in needles, m. p. 65—66°, b. p. 181—182°/15 mm.,  $[\alpha]_D^{18} + 24·20°$  in alcohol. When treated with anhydrous formic or oxalic acid it forms a mixture of two compounds: (1) a *hydrocarbon*,  $C_{10}H_{16}$ :CHPh, b. p. 152—154°/14—15 mm.,  $[\alpha]_D^{18} + 71·89°$  in alcohol,  $n_D^{19}$  1·5472; (2) a *hydrocarbon*,  $C_{17}H_{22}$ , b. p. 163—166°/13—14 mm.,  $[\alpha]_D^{18} - 35·33°$ ,  $n_D^{19}$  1·5694°. W. O. W.

**The Terpinene Question.** KARL AUWERS (*Ber.*, 1909, 42, 2424—2439).—The physical constants of terpinenes prepared from eighteen different sources have been tabulated and subjected to a critical examination. Of the samples under consideration, those prepared by means of terpin cannot be regarded as terpinenes in the sense of the word employed by Wallach to indicate the  $\alpha$ -compound containing the conjugated ethylene linkings, since their optical properties exclude the possibility of their containing more than a trace of this substance. The author is of opinion that not even the carvenene described by Semmler (this vol., i, 110) or the one obtained by Harries and Majima (Abstr., 1908, i, 734) are pure  $\alpha$ -terpinene, but considers that the sample which he prepared from *o-cresol* (compare this vol., i, 592) is very fairly pure. P. H.

**Constituents of Ethereal Oils. Carlina Oxide.** FRIEDRICH W. SEMMLER and EDMUND ASCHER (*Ber.*, 1909, 42, 2355—2360).—Attempts to ascertain whether the chain of three carbon atoms uniting the benzene and the furan rings in carlina oxide (*Abstr.*, 1906, i, 297) contains an acetylenic or a di-olefinic linking have been unsuccessful. When  $\alpha$ -phenyl- $\gamma$ -2-furyl- $\Delta^{\beta}$ -propene- $\alpha$ -one is reduced by sodium and alcohol, the main product, in addition to tetrahydrocarlina oxide, is  $\alpha$ -phenyl- $\gamma$ -2-furylpropane- $\alpha$ -ol,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_4\text{OH}_3$ , b. p. 168—170°/12 mm.,  $D_4^{20}$  1.10,  $n_D$  1.55, which is obtained alone when the reduction is effected by sodium amalgam and acetic acid; the phenylurethane,  $\text{C}_{20}\text{H}_{19}\text{O}_3\text{N}$ , has m. p. 95.5—96°, and the acetate,  $\text{C}_{15}\text{H}_{16}\text{O}_3$ , has b. p. 171—172°/11 mm.,  $D_4^{20}$  1.09,  $n_D$  1.526. The chloride,  $\text{CHPhCl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_4\text{OH}_3$ , b. p. 154°/10 mm.,  $D_4^{18}$  1.13,  $n_D$  1.552, obtained from the alcohol and phosphoric chloride in light petroleum, is converted by boiling alcoholic potassium hydroxide into the ethyl ether,  $\text{OEt}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_4\text{OH}_3$ , b. p. 145—147°/11 mm.,  $D_4^{20}$  1.055,  $n_D$  1.545. Hydrogen chloride can be eliminated from the chloride, however, by three to five hours' heating with anhydrous sodium acetate and glacial acetic acid at 170—180°, whereby  $\alpha$ -phenyl- $\gamma$ -2-furyl- $\Delta^{\alpha}$ -propene (*dihydrocarlina oxide*),  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{C}_4\text{OH}_3$ , is obtained, which has b. p. 146.5—147°/13 mm.,  $D_4^{20}$  1.029,  $n_D$  1.552, and in its physical properties lies intermediate between carlina oxide and tetrahydrocarlina oxide.

A second method for the synthesis of carlina oxide starts with  $\alpha$ -phenyl- $\gamma$ -2-furylpropane- $\alpha$ -y-dione,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_4\text{OH}_3$ , m. p. 69°, b. p. 194—196°/11 mm., which is obtained by Claisen's method (*Abstr.*, 1896, i, 557), gives a blood-red coloration with ferric chloride, and forms an oxime,  $\text{C}_{18}\text{H}_{11}\text{O}_3\text{N}$ , m. p. 137°, and a dioxime,  $\text{C}_{18}\text{H}_{12}\text{O}_3\text{N}_2$ , m. p. 168°. The reduction of the diketone by sodium amalgam and dilute acetic acid, however, does not yield the glycol, but a diacetate,  $\text{C}_{18}\text{H}_{12}\text{O}_5\text{Ac}_2$ , m. p. 149°. C. S.

**Javanese Basilicum Oil and Methylchavicol.** PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 15—16. Compare *Abstr.*, 1901, i, 220).—Distillation in steam and fractionation of this oil ( $D^{14}$  0.962;  $n_D$  + 1°20'/200 mm.) gave a fraction boiling below 88°, which contains cineol and an oil, b. p. 60—70°/in vacuo,  $D^{15}$  0.8208, which probably contains an olefinic terpene (ocimene?).

The methylchavicol obtained from this source is always optically active; this activity is destroyed by treatment with magnesium methyl iodide, but not by acetic anhydride, potassium permanganate, or sodium hydrogen sulphite. Methylchavicol, when heated in a sealed tube for forty-eight hours at 250°, gives two crystalline substances, m. p. 98° and 166°, which appear to be dimolecular isomerides of methylchavicol. The compound of m. p. 98° gives a dibromide,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Br}_2$ , m. p. 87°. W. R.

**Essential Oil from the Fruit of Morinda citrifolia L.** PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 17—19).—This oil ( $D^{18}$  0.927) is remarkable, as it contains 90% of free octoic and hexoic acids, the amount of the latter being approxi-

mately 12% of the free fatty acids present. The neutral volatile constituents consist of the ethyl esters of these acids together with traces of the methyl (?) esters. The crude oil also contains crystals of a saturated hydrocarbon, m. p. 60°, in suspension. W. R.

**Turmeric Oil.** HANS RUPE, E. LUKSCH, and A. STEINBACH (*Ber.*, 1909, 42, 2515—2520. Compare Abstr., 1908, i, 95).—From turmeric oil having  $D_{20}^{20}$  0.9388 and  $[\alpha]_D^{20} - 24.76^\circ$ , the authors have been unable to isolate Jackson and Menke's turmerol. By heating the oil with alcohol and 30% potassium hydroxide, a ketone, *curcumone*,  $C_{13}H_{18}O$ , has been obtained, which has b. p. 121°/10 mm.,  $D_{20}^{20}$  0.9566,  $n_D^{20}$  1.50526,  $[\alpha]_D$  80.55°, forms a *semicarbazone*, m. p. 120—121°, an *oxime*, b. p. 159°/11 mm., a *phenylhydrazone*, m. p. 92°, a *p-bromophenylhydrazone*, m. p. 71°, and condenses with benzaldehyde to form the compound,  $C_{13}H_{16}O:CHPh$ , m. p. 106°, with piperonal to form the compound,  $C_{13}H_{18}O:CH \cdot C_6H_5 \cdot O_2 \cdot CH_2$ , m. p. 86°, and with anisaldehyde to form a similar compound, m. p. 77—78°. C. S.

**Constitution of Bixin.** J. F. B. VAN HASSELT (*Chem. Weekblad*, 1909, 6, 480—483. Compare Etti, Abstr., 1874, 907; 1878, 739; Zwick, Abstr., 1897, i, 630; Marchlewski. Abstr., 1906, i, 760).—A study has been made of the properties of bixin, the red-colouring matter of *Bixa orellana*. Its empirical formula is  $C_{29}H_{34}O_6$ , containing one carbon atom more than that hitherto accepted. It has m. p. 189° (corr.). At 190° it yields *m*-xylene, but no other volatile product. When one gram-molecule is heated in a current of hydrogen at 200°, it loses one gram-molecule of *m*-xylene, but it is not probable that the *m*-xylene nucleus is present as such in the bixin molecule. Zwick's statement that heating for several hours in steam at 160° converts bixin into palmitic acid was not substantiated, no change taking place. The statement of Zwick that bixin contains two carbonyl groups, based on the formation of a condensation product with phenylhydrazine, is also regarded as of doubtful value.

Acids convert solutions of the di-potassium salt into a substance to which the name *norbixin* has been assigned. Unlike bixin, *norbixin* does not contain a methoxyl group. It is a light red mass of microscopic crystals, does not melt, but darkens and decomposes at 240°. It is readily oxidised. Its empirical formula is  $C_{28}H_{32}O_5$ .

Potassium bixinate and methyl sulphate yield diamond-shaped plates of *bixin methyl ether*,  $R(OMe)_2$ , m. p. 156°. On methylation, *norbixin* yields bixin, and then bixin methyl ether. From diethyl sulphate were prepared *bixin ethyl ether*,  $R(OMe) \cdot OEt$ , m. p. 138°; *norbixin monoethyl ether*,  $OH \cdot R \cdot OEt$ , m. p. 176°, and *norbixin diethyl ether*,  $R(OEt)_2$ , m. p. 121°. Methylation of *norbixin monoethyl ether* forms *norbixin methyl ethyl ether*,  $OMe \cdot R \cdot OEt$ , m. p. 149°, isomeric with bixin ethyl ether. *isoBixin*,  $OH \cdot R \cdot OMe$ , is obtained by partial saponification of methylbixin. It forms short, acicular crystals, m. p. 178°.

On reduction with zinc dust in isatin solution, bixin derivatives take up two hydrogen atoms, forming yellow, crystalline compounds. *Dihydrobixin* has m. p. 200°; *dihydrobixin methyl ether*, 174°, and

*dihydroisobixin*, 191°. *Dihydronorbixin* is infusible, and melts at 235°.

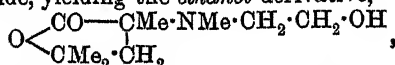
Bixin takes up ten bromine atoms, forming white, amorphous, very unstable bromo-derivatives. Its unsaturated character is also indicated by its reacting with iodine chloride. Both reagents point to the presence of five ethylene linkings. A. J. W.

**History of the Optical Activity of Tannin.** OTTO ROSENHEIM (*Ber.*, 1909, 42, 2452—2453).—The optical activity of tannin was first observed by Ph. van Tieghem, who recorded the fact in *Ann. Sci. Nat.*, 1867, [v], 8, 210. P. H.

**The Lactones of  $\alpha$ -Dihydroxy- $\alpha$ -dimethylvaleric Acid and  $\alpha$ -Methylamino- $\gamma$ -hydroxy- $\alpha$ -dimethylvaleric Acid.** MORITZ KOHN (*Monatsh.*, 1909, 30, 401—406).—The lactone of  $\alpha$ -dihydroxy- $\alpha$ -dimethylvaleric acid (4-hydroxy-5-keto-2:2:4-trimethyltetrahydrofuran) (compare Franke and Kohn, *Abstr.*, 1907, i, 816; Kohn, *Abstr.*, 1908, i, 819) may be prepared by hydrolysing the cyanohydrin of diacetone alcohol ( $\beta$ -methylpentane- $\beta$ -ol- $\delta$ -one) with fuming hydrochloric acid; it has m. p. 66—68°, b. p. 230—232°/745 mm.; the b. p. given previously (*loc. cit.*) is incorrect.

*Diacetone alcohol cyanohydrin* cannot be prepared directly from diacetone alcohol, but is obtained as a viscid oil by the action of potassium cyanide on the sodium hydrogen sulphite compound of the keto-alcohol.

4-Methylamino-5-keto-2:2:4-trimethyltetrahydrofuran combines with ethylene oxide, yielding the *ethanol* derivative,



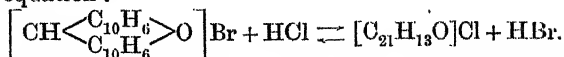
a viscid liquid which could not be crystallised; the *methiodide* is crystalline, and yields the crystalline *aurichloride*,  $\text{C}_{11}\text{H}_{21}\text{O}_3\text{N}_3\text{HAuCl}_4$ , when treated successively with silver chloride and auric chloride.

W. H. G.

**Oxonium Compounds and Pyryl Salts.** ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 692—698).—It is pointed out that the essential difference between oxonium compounds containing the elements of the halogen acids, and pyryl salts is that the former are produced by simple addition of the acid, and thus correspond with ammonium salts (compare Collie and Tickle, *Trans.*, 1899, 75, 710), whilst in the formation of pyryl salts, water is eliminated (Fosse, *Abstr.*, 1901, i, 604, 643; 1902, i, 171, and Werner, *Abstr.*, 1902, i, 50), so that the production of pyryl salts corresponds with the formation of ordinary metallic salts. T. A. H.

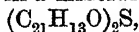
**Metallic Character of an Organic Radicle.** ROBERT FOSSE (*Compt. rend.*, 1909, 148, 1607—1609. Compare *Abstr.*, 1901, i, 604, 643; 1902, i, 51, 171).—The monohalogen derivatives of dinaphthaxanthone resemble certain metallic salts in their behaviour towards mineral acids and towards hydrogen sulphide. Thus the

monobromo-derivative reacts with hydrogen chloride in accordance with the equation :



A similar reversible reaction takes place when picric acid is added to a solution of the chloro-derivative in acetic acid. The *picrate*,  $\text{C}_{27}\text{H}_{15}\text{O}_8\text{N}_3$ , is deposited in reddish-violet crystals, m. p. above  $220^\circ$  (decomp.).

When hydrogen sulphide is passed into a solution of one of the salts of dinaphthaxanthone in a mineral acid, the *sulphide*,



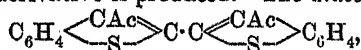
is precipitated. This is decomposed by boiling halogen acids into hydrogen sulphide and a halogen salt of dinaphthaxanthone.

W. O. W.

**Reduction of the Thiophen Nucleus ; a Correction.** VICTOR THOMAS (*Bull. Soc. chim.*, 1909, [iv], 5, 736).—The supposed reduction of thiophen by the Sabatier and Senderens method (this vol., i, 251) is erroneous. Pure thiophen is not reduced, and the benzene previously detected in the products of the reaction is to be attributed to impurities in the thiophen used.

E. H.

**Derivatives of "Thioindigo."** BÉCHAMP (*Compt. rend.*, 1909, 148, 1677—1679. Compare this vol., i, 425).—"Thioindigo" [2:2'-bisoxythionaphthen] undergoes reduction when treated with an organo-magnesium halide; the product after treatment with water is a white substance, which rapidly reverts to "thioindigo"; when the decomposition is effected by acetyl or benzoyl chloride, however, an acetyl or benzoyl derivative is produced. The *diacetyl* derivative,



forms colourless needles, m. p.  $248^\circ$  (decomp.); the *monobenzoyl* derivative,  $\text{C}_{16}\text{H}_9\text{O}_2\text{S}_2 \cdot \text{COPh}$ , forms slender needles, m. p.  $225^\circ$  (decomp.), which oxidise on exposure to air. These derivatives are identical with the substances obtained when "thioindigo" is reduced with tin and hydrochloric acid and then treated with acetic anhydride or benzoyl chloride.

W. O. W.

**A New Alkaloid from the Bark of Pseudocinchona Africana (Rubiaceae).** ERNEST FOURNEAU (*Compt. rend.*, 1909, 148, 1770—1772).—The author describes the preparation and properties of a new monobasic alkaloid from *Pseudocinchona africana* (Perrot, *Compt. rend.*, 1909, 148, 1465). The compound is isomeric with quebrachine, and has the formula  $\text{C}_{21}\text{H}_{26}\text{O}_3\text{N}_2$ ; it crystallises from absolute alcohol in anhydrous, hexagonal tablets, or from dilute alcohol in elongated spangles containing water of crystallisation. On the Maquenne block it melts below  $200^\circ$ , then solidifies, and again melts at  $241$ — $242^\circ$ ; a 2% solution in alcohol has  $[\alpha]_D^{25} - 125^\circ$ . A solution in concentrated sulphuric acid rapidly becomes brown; on the addition of a crystal of potassium dichromate a black film is formed and deep blue streaks are seen in the liquid. The *hydrochloride* crystallises from alcohol in

hexagonal leaflets, m. p. 285—290°, or from water in prismatic needles containing 2 to 3  $\text{H}_2\text{O}$ ;  $[\alpha]_D - 63^\circ$ . The normal *sulphate* forms brilliant, acicular, hexagonal prisms very soluble in water. The *tartrate* crystallises in rectangular tablets; the *methiodide* in prismatic needles, m. p. above 300°. W. O. W.

**Alkaloids of *Dicentra pusilla*.** Y. ASAHINA (*Arch. Pharm.*, 1909, 247, 201—212).—This Japanese plant has been found to contain protopine, a new alkaloid, dicentrine, and a yellow colouring matter, which appears to be identical with *isorhamnetin* (Perkin and Hummel, *Trans.*, 1896, 69, 1568).

The finely ground plant was extracted with alcohol containing acetic acid, and the concentrated extract poured into dilute acetic acid. On shaking the filtrate with ether, the latter extracted a substance crystallising in slender, yellow needles, and having the composition and properties of *isorhamnetin* and yielding a similar tetra-acetyl derivative (*loc. cit.*).

The acetic acid filtrate on addition of a slight excess of ammonia solution gave a dirty greenish-yellow precipitate, which was purified somewhat by re-precipitation several times and then dried and fractionally crystallised from ether. The first fraction consisted of protopine, which Gadamer had already found in *Dicentra spectabilis* (Abstr., 1902, i, 52) and Heyl in *D. formosa* (Abstr., 1903, i, 716). The later fractions consisted of *dicentrine*,  $\text{C}_{20}\text{H}_{21}\text{O}_4\text{N}$ , m. p. 168—169°,  $[\alpha]_D + 62.1^\circ$  in chloroform, which forms prismatic crystals,  $a:b:c = 0.7673:1.0000:0.4424$ , from ether, alcohol, or ethyl acetate. The *hydrochloride*, *hydrobromide*, and *nitrate* are all crystalline, as is also the *platinichloride*, although the last-mentioned salt cannot be re-crystallised from water or alcohol. The *aurichloride* is very unstable. The *methiodide*,  $\text{C}_{20}\text{H}_{21}\text{O}_4\text{N}, \text{MeI}, \text{H}_2\text{O}$ , m. p. 224°, crystallises from dilute alcohol. Dicentrine contains two methoxyl groups, and yields a *monoacetyl* derivative, m. p. 202°, which forms colourless leaflets and is not hydrolysed by potassium hydroxide in alcohol even on boiling. Dicentrine resembles closely the alkaloid, m. p. 168.5—169°, previously obtained by Heyl (*loc. cit.*). T. A. H.

**$\psi$ -Morphine.** GABRIEL BERTRAND and V. I. MEYER (*Compt. rend.*, 1909, 148, 1681—1683. Compare Polstorff, Abstr., 1880, 408; Hesse, Abstr., 1884, 616).—Determinations of the molecular weight of  $\psi$ -morphine by the cryoscopic or ebullioscopic methods are valueless, owing to the tendency of the substance to molecular association; the hydrochloride, on the other hand, undergoes dissociation in aqueous solution, and gives values for the molecular weight which are in agreement with Hesse's formula for the base,  $\text{C}_{34}\text{H}_{36}\text{O}_6\text{N}_2$ . The molecular weight of the acetyl derivative also agrees with this formula. The author considers that  $\psi$ -morphine arises by elimination of two atoms of hydrogen from 2 mols. of morphine, followed by union of the two morphine residues through two carbon atoms. The optical properties of the substance suggest that the two morphine residues are not symmetrically arranged with respect to one another.

W. O. W.

**Strychnos Alkaloids. IV. Reactions of Strychninonic Acid and Fission of the Strychnine Molecule.** HERMANN LEUCHS and WILHELM SCHNEIDER (*Ber.*, 1909, 42, 2494—2499).—In its reactions strychninonic acid (Abstr., 1908, i, 564) closely resembles brucinonic acid (this vol., i, 253). It yields a neutral monoethyl ester, and also an oxime and semicarbazone. The *ethyl* ester,  $C_{23}H_{24}O_6N_3$ , crystallises from hot alcohol in colourless prisms, m. p. 209—210° (corr.). The *oxime*,  $C_{21}H_{21}O_6N_3 \cdot H_2O$ , crystallises from hot water in rectangular prisms, loses its water of crystallisation at 135° under reduced pressure, and has m. p. 268—271° (decomp.). Its alkaline solution has  $[\alpha]_D^{20} + 119^\circ$ . The *semicarbazone*,  $C_{22}H_{23}O_6N_3$ , forms long, slender needles, m. p. 256—257° (corr.). When reduced with sodium amalgam, the acid yields *strychninolic acid*,  $C_{21}H_{22}O_6N_2$ , which crystallises from water in long prisms, m. p. 238°.

*Acetylstrychninolic acid*,  $C_{23}H_{24}O_6N_2$ , crystallises from 50% acetic acid in long needles, m. p. 281° (corr.). When a solution of the reduced acid in *N*-sodium hydroxide solution is kept for several hours, glycollic acid and *strychninolone*,  $C_{19}H_{18}O_3N_2$ , are formed. The latter crystallises from alcohol in glistening prisms, or from hot water in colourless, six-sided plates, m. p. 236° and  $[\alpha]_D^{20} - 112.4^\circ$ .

The conclusion is drawn that strychninonic acid contains the grouping  $C_{17}H_{18}(:N \cdot CO)(:N)(CO_2H)_2(CO)$ . J. J. S.

**Pyrrrole.** EUGEN KHOTINSKY (*Ber.*, 1909, 42, 2506—2507).—By saturating a mixture of ammonium mucate and excess of glycerol with dry ammonia at 270°, and then distilling at 320—330°, and redistilling the distillate, the author has obtained a 41.6% yield of pyrrrole.

C. S.

**Equilibrium in the System: Silver Chloride and Pyridine.** LOUIS KAHLENBERG and WALTER J. WITTICH (*J. Physical Chem.*, 1909, 13, 421—425).—The solubility of silver chloride in pyridine has been determined from the melting point of pyridine to 110°. The eutectic temperature lies at -56°; from -56° to -22° the solubility gradually increases, the solid in equilibrium with the solution being the compound  $AgCl \cdot 2C_5H_5N$ . From -22° to -1° the solubility continues to increase with the temperature, the solid in equilibrium with the solution being a second compound,  $AgCl \cdot C_5H_5N$ , occurring in small, needle-shaped crystals. From -1° to 110° the solution is in equilibrium with silver chloride, and the solubility steadily diminishes as the temperature rises, becoming almost zero at the higher temperature. G. S.

**Electrolysis of Quaternary Pyridinium and Quinolinium Salts.** BRUNO EMMERT (*Ber.*, 1909, 42, 1997—1999. Compare this vol., i, 376).—By the electrolysis of benzylpyridinium chloride between platinum electrodes in sodium carbonate solution, dibenzylidihydrodipyridyl (compare Hofmann, Abstr., 1881, 921) is formed. Seemingly, the unsaturated complex  $C_8H_5N \cdot CH_2 \cdot C_8H_5$  is first formed

in this the nitrogen tends to become tervalent, and in so doing frees a carbon valency in the pyridine nucleus with the result that two such nuclei unite. It is not yet established whether this takes place in the 2, 3, or 4-position.

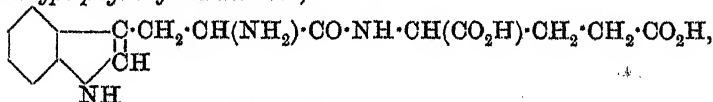
Similarly, methylquinolinium iodide forms *dimethyldihydrodiquinolyl*, and ethylquinolinium iodide gives *diethyldihydrodiquinolyl*. Both are microcrystalline, and reduce silver nitrate on warming. E. F. A.

**Polypeptides containing *l*-Tryptophan.** EMIL ABDERHALDEN (*Ber.*, 1909, 42, 2331—2336. Compare *Abstr.*, 1908, i, 932).—*l*-Leucyl-*l*-tryptophyl-*d*-glutamic acid has been synthesised for comparison with the polypeptide composed of leucine, tryptophan, and glutamic acid, obtained by the partial hydrolysis of edestin. The two peptides have many properties in common, but differ in that the synthetic product is not precipitated by tannin from aqueous solution, and is sparingly soluble in cold water, whereas the analytical product gives a dense precipitate with a tannin solution insoluble in excess, and is easily soluble in water. The synthetic peptide has  $[\alpha]_D^{20} + 17.4^\circ$ ; the analytic compound,  $[\alpha]_D^{20} + 8.2^\circ$ .

A dipeptide composed of tryptophan and glutamic acid was also isolated from edestin, and is now compared with *l*-tryptophyl-*d*-glutamic acid. The two peptides are very similar; the synthetic product, however, has m. p.  $173^\circ$ ,  $[\alpha]_D^{20} + 34.35^\circ$ ; the analytic product, m. p.  $162^\circ$ ,  $[\alpha]_D^{20} + 19.8^\circ$ . It is considered that the analytic product is possibly a mixture.

The tripeptide was synthesised both by converting *l*-leucyl-*l*-tryptophan into the chloride and coupling this with *d*-glutamic acid, whereby only small quantities of an amorphous product were obtained, and also by coupling *l*-tryptophyl chloride and *d*-glutamic acid to the dipeptide, *l*-tryptophyl-*d*-glutamic acid, coupling this further with *d*-bromoisohexoyl chloride, and converting the bromo-compound formed, by means of aqueous ammonia, into the tripeptide. The *d*-glutamic acid was prepared from gliadin; the *l*-tryptophan obtained from the digestion of casein with pancreatin; it is convenient to decompose the mercury sulphate precipitate with barium sulphide.

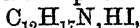
*l*-Tryptophyl-*d*-glutamic acid,



forms minute, colourless needles, which sinter at  $170^\circ$ , m. p.  $173^\circ$  (corr.), and have  $[\alpha]_D^{20} + 34.35^\circ (\pm 0.2^\circ)$ . It gives precipitates with phosphotungstic acid and tannin, soluble in excess of the reagents. *d*- $\alpha$ -Bromoisohexoyl-*l*-tryptophyl-*d*-glutamic acid was obtained as an oily product, which subsequently gave a hygroscopic solid. On hydrolysis with 25% aqueous ammonia at  $37^\circ$ , it was converted into *l*-leucyl-*l*-tryptophyl-*d*-glutamic acid, which crystallises in macroscopic plates aggregated in clusters; these sinter at  $224^\circ$ , m. p.  $230^\circ$  (corr.). It gives a precipitate with mercury sulphate, phosphotungstic acid, and ammonium sulphate, but none with tannin, and shows a violet-red biuret reaction. It has  $[\alpha]_D^{20} + 17.4^\circ (\pm 0.2^\circ)$ . E. F. A.

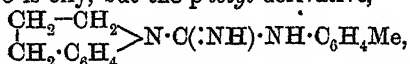
**Relative Stabilities of the Piperidine and Tetrahydroquinoline Rings.** JULIUS VON BRAUN (*Ber.*, 1909, 42, 2219—2227. Compare this vol., i, 507).—A study of the behaviour of cyanogen bromide towards ethylpiperidine and ethyl tetrahydroquinoline, propylpiperidine, and propyltetrahydroquinoline indicates that the piperidine ring is ruptured about twice as easily as the tetrahydroquinoline ring.

1-Propyltetrahydroquinoline,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{N}(C_3H_7) \end{smallmatrix} CH_2$ , obtained from tetrahydroquinoline and propyl iodide, has b. p. 146°/16 mm. The *picrate*,  $C_{12}H_{17}N \cdot C_6H_5O_7N_3$ , has m. p. 73°; the *hydriodide*,



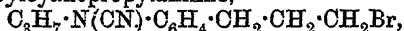
crystallises from water in brilliant needles, m. p. 178°; the *hydrobromide* has m. p. 177°, and the *hydrochloride*, m. p. 162°. When heated on the water-bath with cyanogen bromide, the propyl derivative yields propyl bromide, cyanotetrahydroquinoline, and *o*- $\gamma$ -bromopropylecyanopropylaniline.

1-Cyanotetrahydroquinoline,  $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{N}(\text{CN}) \end{smallmatrix} CH_2$ , is a colourless oil, b. p. 185—188°/17 mm., and, when boiled with acid, yields tetrahydroquinoline, and with bases yields guanidine derivatives. The *phenyl* derivative is oily, but the *p*-tolyl derivative,



obtained by heating the cyano-compound with *p*-toluidine hydrochloride at 150°, crystallises from ether in brilliant, colourless needles, m. p. 180°.

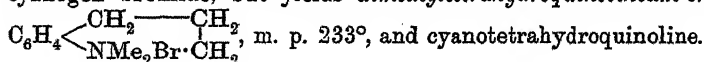
*o*- $\gamma$ -Bromopropylecyanopropylaniline,



could not be isolated.

1-Ethyltetrahydroquinoline has b. p. 134—135°/16 mm., and the *picrate*,  $C_{11}H_{15}N \cdot C_6H_5O_7N_3$ , has m. p. 122°.

1-Methyltetrahydroquinoline is not ruptured when heated with cyanogen bromide, but yields *dimethyltetrahydroquinolinium bromide*,



J. J. S.

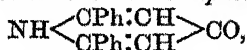
**Rupture of Cyclic Bases by Hofmann's Method.** JULIUS VON BRAUN (*Ber.*, 1909, 42, 2532—2538).—Having shown previously that cyanogen bromide breaks the ring in tertiary bases of the piperidine and tetrahydroquinoline series containing ethyl, propyl, butyl, or an aromatic group attached to the nitrogen, but not in those containing methyl or an unsaturated radicle (*Abstr.*, 1907, i, 960; this vol., i, 507; preceding abstract), the author has investigated the rupture of these bases by Hofmann's method of exhaustive methylation and distillation. It is known that 1-methyltetrahydroquinoline, by successive treatment with methyl iodide, silver oxide, and distillation, regenerates itself. Since 1-ethyltetrahydroquinoline methiodide and 1-propyltetrahydroquinoline methiodide, m. p. 135°, under these conditions yield a mixture of 1-methyltetrahydroquinoline and 1-ethyl-

tetrahydroquinoline or 1-propyltetrahydroquinoline, it appears that tertiary tetrahydroquinolines containing an alkyl group are not ruptured by Hofmann's method. In the piperidine series there seems to be a periodic relation between ease of rupture and the magnitude of the alkyl group attached to the nitrogen atom, for whereas 1-methylpiperidine is completely ruptured by the preceding treatment, the ethyl homologue is not, the propyl compound only very slightly (the main products being the original tertiary base and 1-methylpiperidine), the butyl compound is very largely ruptured, and the *iso*-amyl compound only partly. A plausible explanation of this behaviour cannot yet be found. C. S.

**Synthesis of 6:7-Dimethoxyisoquinoline.** LEOPOLD RÜGHEIMER and P. SCHÖN (*Ber.*, 1909, 42, 2374—2377. Compare Pictet and Kay, this vol., i, 513).—Veratrylaminoacetal (*Abstr.*, 1908, i, 153) is added slowly to a mixture of concentrated sulphuric acid and arsenic acid cooled by ice and salt, and after one hour the mixture is heated on the water-bath. The resulting 6:7-dimethoxyisoquinoline is liberated by sodium hydroxide, removed by ether, and purified by means of the hydrochloride. It appears to be identical with the substance of the same composition obtained by Goldschmiedt by the oxidation of papaverine (*Abstr.*, 1888, 302). C. S.

**Condensation of Esters of Acetonedicarboxylic Acid with Aldehydes by means of Ammonia and Amines.** PAVEL PETRENKO-KRITSCHENKO and S. SCHÖTTLE (*Ber.*, 1909, 42, 2020—2025. Compare *Abstr.*, 1906, i, 452; 1907, i, 708; 1908, i, 564).—Ethyl 2:6-diphenylpiperidone-3:5-dicarboxylate (*loc. cit.*) possesses acid characters and forms a *potassium* salt, m. p. 300°.

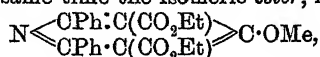
When kept for a time in alkaline solution, and then precipitated with acid, the ester is obtained in a form, m. p. 145—150°. On crystallisation, the melting point rises gradually to the normal (195°). The isomeride is probably the unstable enolic form. When hydrolysed and heated at 258°, the ester forms 2:6-diphenyl-4-pyridone,



m. p. 176—178°. This is still acidic, and forms a *potassium* salt, m. p. 114—140°; the *hydrochloride* has m. p. 249—253°; the *platinichloride*, m. p. 218—221°. The above dicarboxylic acid, when mixed with zinc dust and distilled, forms 2:6-diphenylpyridine, m. p. 81—82°, identical with that described by Scholtz (*Abstr.*, 1895, i, 563).

**4-Chloro-2:6-diphenylpyridine**,  $\text{N} \begin{array}{c} \diagup \text{CPh:CH} \\ \diagdown \text{CPh:CH} \end{array} \text{COCl}$ , prepared by mixing diphenylpyridone with phosphorus pentachloride, moistening the mass with phosphoryl chloride, heating for two hours at 140—150°, and pouring into water, is obtained in needles, m. p. 72°. On repetition of the process, the *dichloride*,  $\text{C}_{17}\text{H}_{13}\text{NCl}_2$ , m. p. 120°, was alone obtained. 2:6-Diphenyl-1-methyl-4-pyridone, treated in a similar manner, forms a monochloride, m. p. 67°, or after treatment with ammonia, m. p. 72°. The last compound when dissolved in benzene and precipitated by hydrogen chloride has m. p. 67°.

*Ethyl 2:6-diphenyl-1-methylpyridone-3:5-dicarboxylate*, prepared by the action of methyl iodide, has m. p. 244°; the corresponding *acid* has m. p. 270°. At the same time the isomeric *ester*, m. p. 189°,



is formed. The corresponding *acid* has m. p. 125°, and when heated with alcoholic potassium hydroxide, it is readily converted into the isomeride, m. p. 270°. E. F. A.

**Cyanodihydrocyclic Amines. I. Acridine Series.** ADOLF KAUFMANN and ALBERTO ALBERTINI [and, in part, MAX HOLSBOER] (*Ber.*, 1909, 42, 1999—2008).—Analogous to the decomposition of quaternary tetramethylammonium cyanide into trimethylamine and acetonitrile, the cyclic ammonium cyanides should give cyanodihydrocyclic amines. The cyanoacridines studied are characterised by their marked crystallising power.

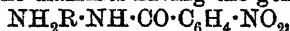
*Acridine methochloride*,  $\text{C}_{13}\text{H}_9\text{N} \cdot \text{MeCl}$ , crystallises in large, well-formed, yellow needles, m. p. 177° (decomp.); the *platinichloride* is a bright yellow, microcrystalline powder, which becomes brown at 230°, and then blackens, m. p. 278—280°; the *mercurichloride* is a yellow, sparingly soluble powder, m. p. 242—244°.

*5-Cyano-10-methyldihydroacridine*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}(\text{CN}) \\ \text{NMe} \end{array} \text{C}_6\text{H}_4$ , prepared by the interaction of acridine methochloride with potassium cyanide, crystallises in colourless needles, m. p. 143°. It has basic properties and forms stable salts; the *platinichloride* separates as long, red needles, decomp. at 200°, which are not yet melted at 280°; the *picrate* crystallises in red needles, m. p. 189°. It is very easily oxidised on warming the alcoholic solution with alkali, or in the cold with hydrogen peroxide, 10-methylacridone being formed.

*5-Phenylacridine methochloride* is a greenish-yellow powder, m. p. 225—226°; the *platinichloride* forms golden-yellow, glistening plates, m. p. 230° to a red liquid; the *mercurichloride* separates as lustrous, yellow needles, m. p. 231°. *5-Cyano-5-phenyl-10-methyldihydroacridine* (compare Hantzsch and Kalb, *Abstr.*, 1900, i, 113) has m. p. 182—183°, and crystallises in long, colourless needles or prisms. It has weak basic properties, forming a *platinichloride*, m. p. 242—243°, which, when heated with hydrochloric acid, is readily converted into the *platinichloride* of phenylacridine methochloride.

*5-Phenylacridine ethiodide* crystallises in well-formed, dark red needles, m. p. 220°. *5-Cyano-5-phenyl-10-ethyldihydroacridine* is obtained in colourless needles, m. p. 140°. The cyano-10-methyldihydroacridines are remarkable stable towards mineral acids, and withstand prolonged heating with concentrated hydrochloric acid without changing. Heating with concentrated sulphuric acid eliminates hydrogen cyanide, and gives rise to the formation of the quaternary sulphate. E. F. A.

[Production of Aromatic Nitrobenzoyldiamines and their Azo-derivatives.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 208968).—The diamines having the general formula



where R is a bivalent aromatic radicle, are produced by treating with *m*- or *p*-nitrobenzoyl chloride the monoformyl derivative of the diamine,  $R(NH_2)_2$ . The formyl group is then readily removed by hydrolysis.

*Nitrobenzoyl-p-phenylenediamine*,  $NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot NH_2$ , lustrous, brownish-golden flakes, m. p.  $228^\circ$ , is prepared by shaking together *p*-nitrobenzoyl chloride and formyl-*p*-phenylenediamine in an aqueous suspension containing some acid-fixing material, such as chalk, sodium carbonate, or sodium acetate, and then hydrolysing the diacylated diamine with dilute hydrochloric or sulphuric acid. The patent contains a tabulated summary of the physical properties of seven other nitrobenzoyldiamines obtained from *p*-phenylenediamine and 2:4-tolylenediamine. These products when diazotised and coupled with 6-amino- $\alpha$ -naphthol-3-sulphonic acid in alkaline solution give rise to nitroazo-compounds, which may be reduced with sodium sulphide, yielding diaminoazo-dyes which dye cotton directly, and on further diazotisation and development on the fibre with  $\beta$ -naphthol give bluish-red colours.

F. M. G. M.

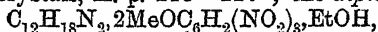
**Condensation of 2-Methylindole with Formaldehyde.** E. VOISENET (*Bull. Soc. chim.*, 1909, [iv], 5, 736—742).—The action of aliphatic and aromatic aldehydes on 2-, 3-, and 7-methylindoles has been studied by Fischer (Abstr., 1888, 283), Freund and Lebach (Abstr., 1903, i, 278; 1905, i, 663), and Renz and Löw (Abstr., 1904, i, 190), but hitherto the aldehydes employed have not included formaldehyde. With the object of elucidating the sensitive colour reaction given by the latter aldehyde with protein substances in the presence of a weak oxidising agent and excess of acid (Abstr., 1906, ii, 59), the author is investigating its condensation with indole and the methylindoles. Unlike other aliphatic aldehydes, formaldehyde condenses quite readily with 2-methylindole. When the latter is treated with commercial formaldehyde, it is converted into *dimethyl-3-methylenedi-indole*,

$CH_2 \left[ C \begin{array}{c} \text{CMe} \\ \text{C}_6H_4 \end{array} > NH \right]_2$ , a colourless substance crystallising from acetone in prisms and from alcohol or ether in needles, which soften at  $230^\circ$  and have m. p.  $240^\circ$ . On exposure to light and air, the crystals become coloured, first orange-red, and then deep red. Dimethylmethylenedi-indole is not decomposed by water; it dissolves in concentrated hydrochloric or glacial acetic acids, but the corresponding salts are too unstable to be isolated, and in the presence of hot concentrated hydrochloric acid, it tends to decompose into methylindole and methylenemethylindole. With platonic or auric chlorides, its hydrochloric acid solution gives a dark grey precipitate, becoming reddish-violet on exposure to air. Dimethylmethylenedi-indole is readily oxidised, when its acetone solution is boiled with an alcoholic solution of chloranil containing a few drops of hydrochloric acid, the magenta-red colouring matter, *dimethylmethylenediroindole*, being produced. The colour of the latter is destroyed by alkalis or reducing agents.

The condensation of formaldehyde with 2-methylindole takes place in the absence of any catalyst, although a trace of formic or other acid accelerates the reaction.

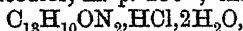
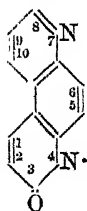
E. H.

**$\psi$ -Phenanthroline.** ADOLF KAUFMANN and RADOSLAV RADOŠEVIĆ [with RICHARD HÜSSY and WULF DAMJE] (*Ber.*, 1909, 42, 2612—2622).—The author suggests replacing the accepted names phenanthroline,  $\psi$ -phenanthroline, and *isophenanthroline* by the terms *m*-phenanthroline, *p*-phenanthroline, and *o*-phenanthroline. A quantitative yield of  $\psi$ -phenanthroline may be obtained by warming on an oil-bath a mixture of 6-aminoquinoline, arsenic acid, glycerol, and concentrated sulphuric acid; by diluting the resulting liquid, and pouring it drop by drop into the calculated quantity of alkali hydroxide, the substance is precipitated in the form of colourless needles free from the resinous impurities commonly met with in this preparation; the anhydrous substance, dried at 110°, crystallises from light petroleum in needles, m. p. 177°. A *mercuric* salt is precipitated from aqueous solutions of  $\psi$ -phenanthroline by the addition of mercuric chloride; it crystallises from dilute hydrochloric acid in feathery aggregates, m. p. 182—185°. The *picrate* forms yellow needles, m. p. 249—250°; the *monomethiodide*, fine yellow needles, m. p. 257° (decomp.); the corresponding *chloride*, yellow needles, m. p. 218—221°; the *methyl picrate*, glistening needles, m. p. 235°; the *dimethiodide*, prepared by the action of potassium iodide on the methyl sulphate additive compound, large, reddish-brown prisms, m. p. 265° (decomp.); the corresponding *chloride*, from the methyl sulphate compound and sodium chloride, stout, brownish-yellow crystals, m. p. 218—220°; the *dipicrate*,



prepared by adding picric acid to an alcoholic solution of the dimethiodide or chloride, forms brown needles, m. p. 233—237°. Attempts to oxidise phenanthroline to the corresponding quinone, or to prepare a nitro-derivative, failed.

**4-Methyl- $\psi$ -phenanthrol-3-one**, annexed formula, obtained by treating  $\psi$ -phenanthroline methiodide with potassium ferricyanide and potassium hydroxide, separates from benzene in faintly yellow crystals, m. p. 239—240°; the *mercuric* salt forms yellowish-brown needles, m. p. 280°; the *hydrochloride*,



yellow needles, m. p. 297—298°; the *nitrate*, yellowish-red needles, m. p. 229—230°; the *methiodide*, obtained from the methylsulphate additive compound and potassium iodide, forms yellow needles, decomposes at 260°, and melts at 294—295°; the *methyl picrate* forms yellow needles and leaflets, m. p. 255°.

**5-Nitro-4-methyl- $\psi$ -phenanthrol-3-one**, prepared by warming phenanthroline nitrate on a water-bath with a mixture of concentrated sulphuric acid and fuming nitric acid, crystallises from alcohol in yellow needles, m. p. 301—303°; forms a *picrate*, m. p. 225°, and a *platinum* salt.

**5-Amino-4-methyl- $\psi$ -phenanthrol-3-one**,  $\text{C}_{13}\text{H}_{11}\text{ON}_2, 2\text{H}_2\text{O}$ , obtained by reducing the last-mentioned nitro-compound with ammonium sulphide, crystallises from water in brownish-yellow needles, m. p. 250°; the *hydrochloride*, red needles, decomposes above 300°; the *acetyl* derivative, silken needles, m. p. 280°; the *picrate*, dark red powder, decomposes at 263°.

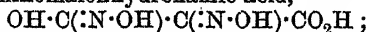
**4:7-Dimethyl- $\psi$ -phenanthroline-3:8-dione**, prepared by oxidising  $\psi$ -phenanthroline dimethiodide with potassium ferricyanide in alkaline

solution, crystallises with  $4\text{H}_2\text{O}$  in glistening needles, and melts above  $320^\circ$ ; when dried in a vacuum over sulphuric acid it loses  $\text{H}_2\text{O}$ , and when heated at  $110$ — $120$  it becomes anhydrous, and is then very deliquescent; it yields no salts. P. H.

**Furoxans. II. Degradation of Ethyl Furoxandicarboxylate (Ethyl Glyoxime-peroxide-dicarboxylate).** HEINRICH WIELAND, LEOPOLD SEMPER, and ERWIN GMEIN (*Annalen*, 1909, 367, 52—79).—Mainly an amplification of work which has been described previously (compare Wieland and Semper, *Abstr.*, 1908, i, 108; Wieland and Gmelin, *ibid.*, 1013).

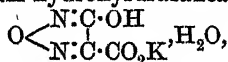
Furoxandicarboxylic acid cannot be obtained by treating the barium salt with acids, since it is very unstable, and dissociates immediately into carbon dioxide and furoxancarboxylic acid,  $\text{O} \begin{smallmatrix} \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \text{N} \cdot \text{O} \cdot \text{N} \end{smallmatrix}$ .

The latter substance is likewise unstable, and readily undergoes hydrolysis, yielding oximinomalonhydroxamic acid,



it is also decomposed by amines with the formation of aminoximes; thus, with aniline it yields oximinomalonanilideoxime (compare Wieland and Gmelin, *loc. cit.*). These changes take place with such ease that the transformation of the carboxylic acid into furoxan appears to be impracticable; even acetic anhydride, which in analogous cases is employed with success to effect the elimination of carbon dioxide, in this case leads to the destruction of the furazan ring.

It is probable that the salt obtained by Nef (*Abstr.*, 1895, i, 9) by hydrolysing oximinocyanoacethydroxamic acid with potassium hydroxide is not potassium hydroxyfuroxancarboxylate,



but potassium oximinomalonhydroxamate.

The authors criticise adversely the work of Jovitschitsch (*Abstr.*, 1906, i, 732). The supposed glyoxime-peroxide-dicarboxylic acid of this investigator is shown to be ethyl hydrogen furoxandicarboxylate, whilst the silver salts described in the same paper are probably mixtures.

Finally, the synthesis of *p*-methoxy- $\alpha$ -isatoxime and 5:5'-dimethoxy-indigotin has been effected by the method of Wieland and Gmelin (*loc. cit.*).

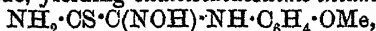
*Barium furoxandicarboxylate*,  $\text{C}_4\text{H}_6\text{N}_2\text{Ba} \cdot \text{H}_2\text{O}$ , crystallises in slender needles, and is extremely explosive when dry. It is converted by a 10% solution of hydrochloric acid ( $1\frac{1}{2}$  mols.) into the *barium hydrogen salt*,  $\text{C}_8\text{H}_2\text{O}_{12}\text{N}_4\text{Ba}$ , crystallising in glistening leaflets. *Silver furoxandicarboxylate*,  $\text{C}_4\text{O}_6\text{N}_2\text{Ag}_2$ , is a pale yellow, highly explosive powder.

*Furoxancarboxylic acid* crystallises in stellate groups of colourless needles, m. p.  $89$ — $91^\circ$  (decomp.); it may be kept for some time in a desiccator, but decomposes rapidly in solution; with calcium chloride it forms an *additive* compound of indefinite composition, obtained as a crystalline powder.

*Oximinomalonhydroxamic acid* is most readily obtained as its *barium*

salt,  $C_3H_2O_5N_2Ba$ , a heavy, pale yellow powder, by treating barium furoxandicarboxylate with excess of barium hydroxide solution; the acid crystallises in aggregates of prisms, m. p.  $135^\circ$  (decomp.). A brownish-green *copper* salt, lemon-yellow *mercurous* salt, pale yellow *lead* salt, and bright yellow, crystalline *silver* salt were prepared. The acid is rapidly decomposed by mineral acids, yielding carbon dioxide, hydroxylamine, and hydrogen cyanide.

*Synthesis of 5:5'-Dimethoxyindigotin.*—Barium furoxandicarboxylate is converted by *p*-anisidine hydrochloride in aqueous solution and subsequent treatment with dilute hydrochloric acid into *oximinomalon-p-anisidideoxime*,  $CO_2H \cdot C(\dot{N} \cdot OH) \cdot C(\dot{N} \cdot OH) \cdot NH \cdot C_6H_4 \cdot OMe$ , which crystallises in white, glistening leaflets, m. p.  $164^\circ$  (decomp.), and is acted on by acetic anhydride at about  $60^\circ$ , yielding *cyanoformanisidideoxime acetate*,  $OAc \cdot N \cdot C(CN) \cdot NH \cdot C_6H_4 \cdot OMe$ , crystallising in short needles, m. p.  $171-172^\circ$  (decomp.). The latter substance reacts with ammonium sulphide, yielding *oxanisidideoxime-thiamide*,



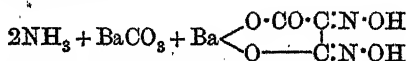
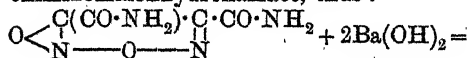
which crystallises in small, pale yellow needles, decomposes at  $174^\circ$ , and, when warmed with fuming sulphuric acid, yields *5-methoxy-*

*2-isatoxime*,  $OMe \cdot C_6H_3 \cdot \begin{smallmatrix} NH \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} \cdot C \cdot N \cdot OH$ , dark red needles with a bronzy

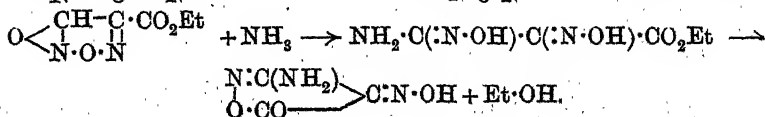
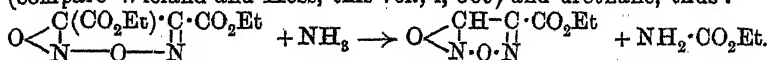
reflex, sintering at  $225^\circ$ , m. p.  $232^\circ$  (decomp.); the *sodium* salt of the latter substance forms glistening, orange-yellow leaflets. *5:5'-Dimethoxyindigotin*,  $C_{18}H_{14}O_4N_2$ , prepared by boiling the methoxyisatoxime with alcoholic ammonium sulphide, crystallises in glistening, dark blue needles and prisms.

W. H. G.

**Furoxans. III. Behaviour of Ethyl Furoxandicarboxylate towards Ammonia and Amines.** HEINRICH WIELAND and ERWIN GMELIN (*Annalen*, 1909, 367, 80-99).—It is shown that the compound formed by the action of ammonia on ethyl furoxandicarboxylate is furoxandicarboxylamide, since it is hydrolysed by an aqueous solution of barium hydroxide, yielding barium carbonate, ammonia, and barium oximinomalonhydroxamate, thus:

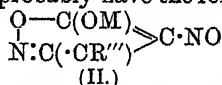
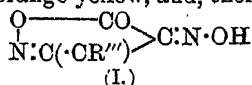


(compare Prpper, Abstr., 1883, 573; Bouveault and Bongert, *Bull. Soc. chim.*, 1902, 27, 1170; Ulpiani and Ferreti, Abstr., 1902, i, 430; Wahl, Abstr., 1908, i, 141). The formation of the amide from the ester is accompanied by the production of amino-oximinoisooxazolone (compare Wieland and Hess, this vol., i, 369) and urethane, thus:



Homologues of amino-oximinoisooxazolone are formed analogously by the action of secondary aliphatic amines on ethyl furoxandicarboxylate (compare Bouveault and Bongert, *loc. cit.*).

Oximinoisooxazolones of the type (I) are colourless, whilst their salts are orange-yellow, and, therefore, probably have the formula (II).



The introduction of the amino-group is accompanied by the production of colour in the free isooxazolone derivatives, whilst the salts have practically the same colour. It is therefore probable that these compounds exist in the nitroso-enolic form, in agreement with which is the fact that they are readily reduced in the cold by zinc dust and dilute acetic acid.

Furoxandicarboxylamide forms colourless needles, m. p. 222—223°: Bouveault gives m. p. 253° (*loc. cit.*).

Cyanomethenylamino-oxime acetate,  $\text{CN}\cdot\text{C}(\text{NH}_2):\text{N}\cdot\text{OAc}$ , is prepared by the action of acetic anhydride on oximinomalonamino-oxime (Wieland and Hess, *loc. cit.*); it forms long, spear-shaped crystals, sinters at 125°, m. p. 137° (decomp.).

Oximinopiperidylisooxazolone,  $\begin{array}{c} \text{O} \quad \text{CO} \\ \parallel \quad \diagup \\ \text{N:C}(\text{C}_5\text{NH}_{10}) \end{array} > \text{C:N}\cdot\text{OH}$ , prepared by the action of piperidine on ethyl furoxandicarboxylate, crystallises in orange-red needles and decomposes at 148°; the piperidine and barium salts are orange-red. It is converted by warm aqueous barium hydroxide into the barium salt of oximinomalonpiperidideoxime; attempts to obtain the corresponding acid were unsuccessful, since it passes immediately into oximinopiperidylisooxazolone; the barium salt is converted by acetic anhydride into cyanopiperidinomethylene-oxime acetate,  $\text{CN}\cdot\text{C}(\text{C}_5\text{NH}_{10}):\text{N}\cdot\text{OAc}$ , which crystallises in long, colourless needles, m. p. 53—54°, and is decomposed by 20% sulphuric acid, yielding acetic acid, hydrogen cyanide, piperidine, and hydroxylamine.

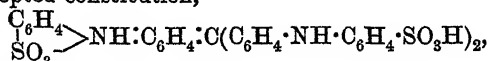
Anilino-oximinoisooxazolone,  $\begin{array}{c} \text{N:C(NHPh)} \\ \parallel \quad \diagup \\ \text{O} \quad \text{CO} \end{array} > \text{C:N}\cdot\text{OH}$ , prepared by the action of hot glacial acetic acid on oximinomalonanilideoxime (compare Wieland and Gmelin, *Abstr.*, 1908, i, 1013), crystallises in dark red, rhombic leaflets and glistening, red needles, and decomposes at 148°.

p-Anisidino-oximinoisooxazolone,  $\text{C}_{13}\text{H}_9\text{O}_4\text{N}_3$ , prepared similarly from the corresponding anisideoxime (preceding abstract), crystallises in glistening, brownish-red leaflets and decomposes at 136°.

Phenylhydrazino-oximinoisooxazolone,  $\begin{array}{c} \text{CO}\cdot\text{C(NOH)} \\ \parallel \quad \diagup \\ \text{O} \quad \text{N} \end{array} > \text{C:NH}\cdot\text{NHPh}$ , prepared by the action of phenylhydrazine on ethyl furoxandicarboxylate, crystallises in small, yellow needles, and decomposes at 183°. It is converted by aqueous alkalis into phenylhydrazideoximecarboxylic acid,  $\text{NHPh}\cdot\text{NH}\cdot\text{C(NOH)}\cdot\text{C(NOH)}\cdot\text{CO}_2\text{H}$ , obtained as an almost colourless substance; the benzoyl derivative,  $\text{C}_{16}\text{H}_{14}\text{O}_5\text{N}_4$ , forms long, yellow needles, sinters at 154°, m. p. 158°.

W. H. G.

**Condition of Some Dyes in Aqueous Solution.** EDMUND KNECHT and J. P. BATEY (*J. Soc. Dyers*, 1909, 25, 194—203).—The widely accepted view that many dyes, particularly those of high molecular weight, exist as colloids in aqueous solution is controverted by the authors. The molecular conductivities at 18° and at 90° of certain acid dyes, such as naphthol-yellow-S, benzopurpurin, soluble-blue, alkali-blue, erica-B, and chrysophenine, indicate that they are good electrolytes, and in dilute solution show a high degree of ionisation. In the trisulphonic acids prepared from Helvetia-blue and spirit-blue, it appears that only two of the three available hydrogen atoms are appreciably ionised, a result which accords with the generally accepted constitution,

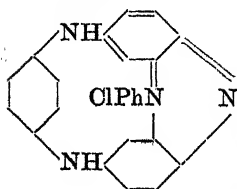


of dyes of this type. The results are confirmed by the ebullioscopic examination of aqueous solutions of naphthol-yellow-S and its calcium salt, soluble-blue, benzopurpurin, and chrysophenine, the molecular weights obtained showing that ionic dissociation has occurred except with naphthol-yellow-S. It is also shown that erica readily diffuses through parchment paper, and that the rates of simple diffusion of benzopurpurin and soluble-blue are high, indicating that they are undergoing ionic dissociation. C. S.

**Chemical Technology of Aniline-Black.** ARTHUR G. GREEN (*J. Soc. Dyers*, 1909, 25, 188—192).—Little definite is known regarding the chemical constitution of aniline-black, owing probably to its being produced exclusively on the fibre and not in substance. In the usual processes of dyeing, the cotton goods are steeped in a solution containing aniline hydrochloride, sodium chlorate, and a copper or vanadium salt or potassium ferrocyanide, and dried; by warming, an intermediate green shade is produced, which passes into black by treating the goods with a solution of sodium dichromate. Three stages of oxidation or condensation are usually distinguished, the predominating compounds being emeraldine, nigraniline, and un-greenable black; commercial aniline-black contains these compounds in variable proportions. Published analyses, which refer mainly to mixtures of emeraldine and nigraniline, are therefore widely divergent, but the balance of evidence favours the composition  $\text{C}_{18}\text{H}_{15}\text{N}_3\text{HCl}$  or  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{HCl}$ . There is little doubt that the aniline residues in the two substances are singly combined by para-nitrogen atoms in chain or ring form, and the constitution  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \\ \text{N} \cdot \text{C}_6\text{H}_4 \end{smallmatrix} > \text{NH}$  for emeraldine harmonises with the production of quinone by oxidation, of only di-*p*-nitrogen derivatives by complete reduction, with the stability of the substance to boiling dilute acids, and with Nietzki's synthesis of aniline-black by the oxidation of a mixture of aniline and di-*p*-aminodiphenylamine, or of diphenylamine and *p*-phenylenediamine. The close relationship of nigraniline chloride,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} : \text{C}_6\text{H}_4 \\ \text{N} : \text{C}_6\text{H}_4 \end{smallmatrix} \gg \text{NCl}$ , to emeraldine is shown by the facts: (1) emeraldine on the fibre is oxidised by cold potassium dichromate or persulphate to nigraniline. The colour of the latter is changed only slightly by acids or alkalis,

since the base and the salts are of the same type; (2) nigraniline on the fibre is reduced by cold sodium hydrogen sulphite to the original green emeraldine, and by further reduction by stannous chloride or sodium hyposulphite to colourless leuco-emeraldine; (3) nigraniline on the fibre, when treated with dilute mineral acids, is partly oxidised to quinone and partly reduced to emeraldine.

In deducing the constitution of ungreenable black, the following particulars must be considered. Ungreenable black is not reduced to emeraldine, and is unaffected by mineral acids, is reduced by sodium hyposulphite to a brown leuco-compound, which readily re-oxidises to the original black, and for its complete production by the further oxidation of emeraldine the presence of aniline or other primary aromatic amine is necessary.



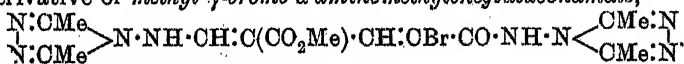
From the facts that the aniline cannot be replaced in the condensation by dimethylaniline, and that *p*-toluidine, which on account of the para-methyl group does not give rise to emeraldine or aniline-black on oxidation, can be employed to convert emeraldine or nigraniline into an ungreenable black, the conclusion is drawn that an unsubstituted amino-group is

concerned in the reaction. The annexed constitution for the chloride of ungreenable black best interprets these facts.

The author also discusses the theory of the oxidation of aniline to aniline-black by atmospheric oxygen in the presence of cupric chloride and *p*-diamines or *p*-aminophenols (Eng. Pat. 1907, 16189, A. G. Green). C. S.

**Action of 1-Amino-1:3:4-triazole and its 2:5-Substitution Products on Methylbromocoumalic Acid.** CARL BÜLOW and FRITZ WEBER (*Ber.*, 1909, 42, 1990—1996).—1-Amino-1:3:4-triazole has been proved to be the parent substance of the so-called *N*-dihydrotetrazines and similar compounds. To support this formula the behaviour of the aminotriazole and its homologues towards methylbromocoumalic acid is now studied. 1-Aminotriazole and the ester condense on heating in alcoholic solution for eight days at 45—55° to *methyl 3-bromo-1(1':3':4')-triazolyl-2-pyridone-5-carboxylate*,  $\begin{matrix} \text{N:CH} \\ \text{N:CH} \end{matrix} > \text{N} \cdot \text{N} < \begin{matrix} \text{CO} \\ \text{CH:C(CO}_2\text{Me)} \end{matrix} \begin{matrix} \text{---COBr} \\ > \text{CH} \end{matrix}$ , the crystals of which are colourless, m. p. 211°, decomp. 212°.

The 1-amino-2:5-dimethyl- or -diphenyl-triazoles could not be made to condense with ethyldiacetylsuccinate, but they combine with methylbromocoumalate, yielding, however, owing to the opening of the  $\alpha$ -pyrone nucleus, derivatives of glutaconic acid. This reaction confirms the view that these 2:5-substitution products of the triazole contain a 1-amino-group. Apparently the activity of the *N*-amino-group of a heterocyclic ring is much reduced by the presence of two neighbouring alkyl groups. 1-Amino-2:5-dimethyl-1:3:4-triazole and methyl bromocoumalate yield the *di-2:5-dimethyltriazolyl* derivative of *methyl  $\gamma$ -bromo- $\alpha$ -aminomethyleneglutaconamate*,



This crystallises in needles, m. p. 205°.

The corresponding *di-2:5-diphenyltriazolyl* derivative separates in colourless, glistening crystals, m. p. 183—183.5°. E. F. A.

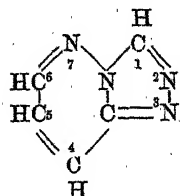
**Triazolepyrrole and Triazolelutidone Derivatives.** CARL BÜLOW and FRITZ WEBER (*Ber.*, 1909, 42, 2487—2494. Compare Abstr., 1906, i, 905; 1907, i, 99; preceding abstract).—1(1':3':4')-*Triazolyl-2:5-dimethylpyrrole-3:4-dicarboxylic acid*,  $C_{10}H_{10}O_4N_4 \cdot H_2O$ , obtained by hydrolysing the corresponding ester (Abstr., 1906, i, 906) with 5% potassium hydroxide solution, crystallises from water in slender, colourless needles, m. p. 290—295° (decomp.). When the acid is titrated with sodium hydroxide in the presence of phenolphthalein, only some 75% of the theoretical amount of alkali is required. When the acid is left in contact with an excess of concentrated ammonium hydroxide solution in a desiccator over sulphuric acid, the *monoammonium* salt,  $C_{10}H_{13}O_4N_5$ , is obtained, which crystallises from water in slender needles, m. p. 280—285° (decomp.). The addition of silver nitrate to a solution of the ammonium salt produces a precipitate of the *silver* salt,  $C_{10}H_9O_4N_4Ag$ .

Diacetylacetone, as a representative symmetrical 1:5-diketone, reacts readily with 1-amino-1:3:4-triazole, yielding 1-triazole-2:6-lutidone,  $N:CH \begin{matrix} N:CH \\ N:CH \end{matrix} > N \cdot N < \begin{matrix} CMe:CH \\ CMe:CH \end{matrix} CO$ , which crystallises from absolute alcohol in colourless needles, melting and decomposing at a temperature above the b. p. of sulphuric acid. It yields a pale blue, crystalline precipitate with copper nitrate, a colourless, crystalline precipitate with silver nitrate, and well-developed crystals with mercuric chloride. Reducing agents have no action on the condensation product.

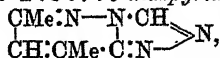
2:5-Dialkylated aminotriazoles do not condense with 1:5-diketones. J. J. S.

**Action of 1-Amino-1:3:4-triazole on Diketones.** CARL BÜLOW and FRITZ WEBER (*Ber.*, 1909, 42, 2208—2216. Compare Abstr., 1906, i, 905; 1907, i, 99; preceding abstract).—1-Amino-1:3:4-triazole condenses with a hot alcoholic solution of diacetyl, yielding the product,  $N:CH \begin{matrix} N:CH \\ N:CH \end{matrix} > N \cdot N \cdot CMe \cdot CO \cdot CH_3$ , which crystallises from alcohol and melts at 197—199°.

1-Amino-1:3:4-triazole condenses with 1:3-diketones, yielding compounds with two condensed heterocyclic nuclei (a 6 and a 5 ring) having a nitrogen and a carbon atom in common (annexed formula).



4:6-Dimethyl-2:3:7:0-diazpyridazine.



obtained by condensing an alcoholic solution of acetylacetone with aminotriazole in the presence of a few drops of piperidine, crystallises from a mixture of benzene and light petroleum, and has m. p. 122—123°. The compound is volatile without decomposition, and forms a *nitrate*,

$C_7H_8N_4HNO_3$ , which crystallises in colourless needles, m. p. 180—181° (decomp.).

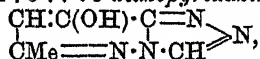
4:5:6-Trimethyl-2:3:7:0-diazpyridazine,  $\begin{array}{c} \text{CMe:N—N·CH} \\ \text{CMe:CMe·C=N} \end{array} \gg \text{N}$ , obtained from methyl acetylacetone and aminotriazole, has m. p. 129°, and crystallises from hot water, in which it is readily soluble, in long, glistening needles.

Benzoylacetone and 1-aminotriazole yield 4-phenyl-6-methyl-2:3:7:0-diazpyridazine,  $\begin{array}{c} \text{CMe:N—N·CH} \\ \text{CH:CPh·C=N} \end{array} \gg \text{N}$ , which crystallises from a mixture of benzene and light petroleum in colourless, slender needles, m. p. 152—153°. It forms additive compounds with cupric nitrate and mercuric chloride.

The condensation products are all strong poisons; they yield characteristic additive compounds with many metallic salts, and also form salts with certain acids. J. J. S.

**Synthesis of Heterocyclic Dinuclear Compounds: Heterohydroxylic Acids.** CARL BÜLOW [and FRITZ WEBER] (*Ber.*, 1909, 42, 2594—2603. Compare preceding abstract).—The pyridazine derivatives described in this paper have marked acid properties, comparable with those of the true carboxylic acids, and it is proposed to call them heterohydroxylic acids.

4-Hydroxy-6-methyl-2:3:7:0-diazpyridazine,



obtained by boiling together ethyl acetoacetate and aminotriazole for eight hours in glacial acetic acid solution, separates from alcohol in slender, colourless needles, which melt above the boiling point of sulphuric acid; in alcoholic solution it gives a claret-red colour with ferric chloride; the substance is soluble in potash, and can be titrated by means of phenolphthalein; when dissolved in water and treated with silver nitrate or mercuric chloride, it gives an amorphous silver salt or a crystalline mercuric salt; from the sodium salt, the manganous, zinc, nickel, cobalt, copper, lead, mercurous, mercuric, and silver salts have been prepared by double decomposition; their composition may be expressed by the formula  $C_6H_5N_4O \cdot OX$ , in which X represents the metal.

4-Hydroxy-5:6-dimethyl-2:3:7:0-diazpyridazine,  $C_6N_4HMe_2 \cdot OH$ , obtained by boiling together aminotriazole, methyl acetoacetate, and glacial acetic acid for forty-eight hours, crystallises from water in small, snow-white needles, m. p. 252°; its sodium salt gives a number of characteristic precipitates with various metallic salts; the precipitates in many cases differ from those obtained by the interaction of the aqueous solution of the free acid with the same salts.

4-Hydroxy-6-phenyl-2:3:7:0-diazpyridazine,  $C_5N_4H_2Ph \cdot OH$ , prepared by heating a mixture of aminotriazole, ethyl benzoylacetate, and glacial acetic acid for eighteen hours, crystallises from methyl alcohol in colourless needles, m. p. 282°; this substance has also

marked acid properties, and its sodium salt likewise gives characteristic precipitates with most metallic salts.

By boiling together slightly different proportions of aminotriazole, ethyl benzoylacetate, and glacial acetic acid for forty-eight hours, a pure white, crystalline substance, m. p. 243—244°, is obtained of the empirical formula  $C_{15}H_{14}O_2N_8$ ; it appears to be a compound of hydroxyphenyldiazopyridazine,  $C_{11}H_8ON_4$ , with 1-acetylaminotriazole,  $C_4H_6ON_4$ ; whereas the compound  $C_{11}H_8ON_4$ , m. p. 282°, gives in dilute alcoholic solution an immediate claret-red colour with ferric chloride, this substance,  $C_{15}H_{14}O_2N_8$ , m. p. 243—244°, produces under the same conditions only a faint colour change; the more fusible substance is, however, easily converted into the less fusible by boiling for half an hour with ethyl alcohol, or more rapidly by dissolving it in dilute aqueous alkali and precipitating with a slight excess of acetic acid.

P. H.

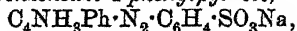
**Reduction of Triphenylmethane Dyes and of Azo-compounds by Sodium Hyposulphite.** OTTO FISCHER, ADOLF FRITZEN, and S. EILLES (*J. pr. Chem.*, 1909, ii, 79, 562—568).—The reducing action of sodium hyposulphite is greatly accelerated by the addition of a little zinc dust. Crystal-violet, malachite-green, and *p*-rosaniline in hot alcoholic solution are reduced to the leuco-bases, whilst 1-benzeneazo-2:2'-dinaphthylamine in alcoholic-pyridine solution yields 1-amino-2:2'-dinaphthylamine, the *acetyl* derivative of which,  $C_{22}H_{18}ON_2$ , has m. p. 214°.

C. S.

**Azopyrroles and their Reduction.** EUGEN KHOTINSKY and MAX SOLOWEITSCHIK (*Ber.*, 1909, 42, 2508—2515).—Various azopyrroles have been prepared and reduced with the hope of obtaining stable aminopyrroles; the latter are formed, but have not been isolated.

*Di-4:4'-a-pyrrolylazodiphenyl*,  $C_{12}H_8(N_2 \cdot C_4NH_4)_2$ , obtained by coupling diazotised benzidine hydrochloride and pyrrole in aqueous-alcoholic solution at 0° in the presence of sodium acetate, is a yellowish-brown powder, which decomposes on heating. The corresponding compound from *o*-tolidine,  $C_{12}H_8Me_2(N_2 \cdot C_4NH_4)_2$ , prepared below -6°, is light brown, and has m. p. 160—165° (decomp.). *2-Benzeneazo-5-phenylpyrrole*,  $C_4NH_2Ph \cdot N_2Ph$ , m. p. 112°, is brownish-yellow, whilst the sodium salt of *2-p-sulphobenzeneazo-5-phenylpyrrole*, obtained by salting out the solution obtained by coupling 2-phenylpyrrole and diazotised sulphanilic acid, is greyish-brown and carbonises without melting. *Di-4:4'-a-phenylpyrrolylazodiphenyl*,  $C_{12}H_8(N_2 \cdot C_4NH_2Ph)_2$ , is a dark red substance, which carbonises without melting, whilst the *N*-phenyl isomeride, m. p. 178°, is brick-red and has more pronounced basic properties. *Di-4:4'-N-phenylpyrrolyl-o-ditolyl*,  $C_{12}H_8Me_2(N_2 \cdot C_4NH_2Ph)_2$ , is dark red, and carbonises at 115°.

*Sodium 2-p-sulphobenzeneazo-1-phenylpyrrole*,

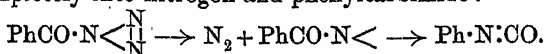


obtained by coupling diazotised sulphanilic acid and 1-phenylpyrrole in glacial acetic acid, and subsequent treatment with sodium carbonate,

forms golden-brown crystals containing  $3\text{H}_2\text{O}$ , which carbonise at  $275\text{--}285^\circ$ .

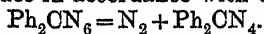
The preceding disazo-compounds are unsuited for reduction on account of their instability, but the sulphonated compounds, particularly the last, can be reduced by stannous chloride and hydrochloric acid or by sodium hyposulphite; the aminopyrroles, however, have not been isolated. C. S.

**The Hofmann-Curtius, Beckmann, and Benzilic Acid Inter-molecular Rearrangements.** GEORG SCHROETER (*Ber.*, 1909, 42, 2336—2349).—Benzoylazouimide, when heated at  $70^\circ$ , decomposes nearly completely into nitrogen and phenylcarbimide:



*o*-Nitrobenzazouimide, when heated at  $50^\circ$ , decomposes in a similar manner into nitrogen and *o*-nitrophenylcarbimide. Neither benzonitrile oxide nor its polymerisation products, diphenylglyoxime peroxide or tribenzonitrile oxide, could be detected as intermediate products of the decomposition of benzazouimide.

Benzophenone chloride reacts with sodium azouimide in cold methylicalcoholic solution to form benzophenonedimethylacetal, m. p.  $107^\circ$ . In amyl ether, however, it reacts with silver azouimide, forming an oil, which decomposes on heating at  $115\text{--}116^\circ$  in a stream of carbon dioxide, liberating nitrogen, and consists in part of benzophenonediazouimide. Decomposition takes place in accordance with the equation:



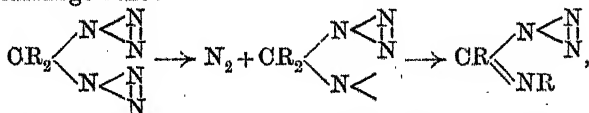
About one-third of the benzophenone chloride is converted into diazouimide and two-thirds into benzophenone, ammonia, and silver chloride.

The compound  $\text{Ph}_2\text{CN}_4$  is 1:5-diphenyl-1:2:3:4-tetrazole,



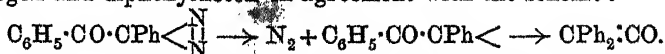
it crystallises in broad, colourless needles, m. p.  $146^\circ$ .

This reaction is in accord with the following scheme for the Beckmann rearrangement:



the alkyliminoazouimide finally undergoing rearrangement to the stable tetrazole.

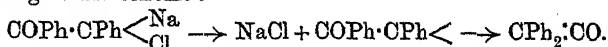
Azibenzil (benzoylphenylazomethylene) in benzene solution, when warmed at  $50\text{--}60^\circ$  in a stream of carbon dioxide, decomposes into nitrogen and diphenylketen in agreement with the scheme:



This forms a very convenient method of preparing diphenylketen. The transformation of dibenzoylstilbene into tetraphenylcrotonolactone and of dibenzoylstryene into triphenylcrotonolactone are explained by similar schemes.

[With CARL CASPAR.]—Desyl chloride, m. p. 68.5°, is conveniently obtained by warming benzoin with the equivalent quantity of thionyl chloride. When distilled under reduced pressure, slight decomposition takes place, and a green vapour is formed, condensing to a green liquid, but which loses its colour when solid and yields pure colourless desyl chloride when crystallised.

Desyl chloride forms a sodium salt, which on warming in benzene solution loses sodium chloride and undergoes rearrangement in part according to the scheme:



E. F. A.

The Changes in Physical Conditions of the Colloids. VIII. Studies on Acid Albumin. WOLFGANG PAULI and HANS HANDOVSKY (*Biochem. Zeitsch.*, 1909, 18, 340—371).—Measurements were made by means of the Ostwald viscometer of the internal friction of "amphoteric" protein solutions which had been prepared by prolonged dialysis of serum of different origins. It was found that the addition of acids increased the viscosity up to a certain concentration, after which further addition caused a decrease in this factor. In the case of weak acids, however, such as acetic and citric acids, the maximum of viscosity was not attained. Addition of salts to the acid proteins diminished the viscosity, and the authors have investigated quantitatively the effect of various salts in producing this diminution. They give in some detail a theory to account for the changes in the properties of the "amphoteric" proteins produced by the action of

acids and salts, which is founded on the assumption that the increased friction is due to the protein ion. By means of acids, the "amphoteric" protein is converted into the "ionised" protein according to the annexed scheme. From the latter formula, salts can be

formed with acids, such as  $\text{R} \begin{smallmatrix} \text{NH}_2 \\ \text{CO}_2\text{H} \end{smallmatrix} \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$ , which can give rise to the

ions  $\text{Cl}^-$  and  $\text{R} \begin{smallmatrix} \text{NH}_3^+ \\ \text{CO}_2\text{H} \end{smallmatrix}$ . Addition of hydrochloric acid to solutions containing such ions will depress the dissociation, and thus diminish the amount of protein ion and the viscosity. The action of salts is also ascribed to the decrease of the protein ions in solution, resulting from interaction of the protein salt with the added salt, which action the authors discuss in some detail.

S. B. S.

The Electric Charge of Serum Albumin and of Ferments. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 19, 181—185).—The earlier experiments of Hardy and of Pauli on the behaviour of serum-albumin in an electric field left it doubtful whether any migration takes place. This was a result of the apparatus employed by these authors, which did not completely exclude the formation of acid and alkali at the electrodes. By using the arrangement employed by the

present author in his work on ferments (this vol., i, 277), this is avoided, and the solution remains neutral throughout; in such a solution the proteins migrate exclusively to the anode. In that case the concentration of hydrogen ions is  $10^{-7}$ ; with one part of acetic acid in 10,000 ( $H^+ = 10^{-5}$ ), the migration is purely cathodic. The intermediate concentration of hydrogen ions ( $H^+ = 10^{-6}$ ) was obtained by sodium phosphate; in it the albumin wandered to both electrodes (compare also Pauli and Handovsky, preceding abstract). G. B.

**Refractive Indices of Solutions of the Caseinates and the Acid and Alkali Equivalents of Casein.** T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1909, 13, 469—489).—The refractive indices of solutions which differ only in their casein-content are connected by the formula  $n - n_1 = ac$ , where  $n$  is the observed refractive index of the solution,  $c$  is the concentration of the casein,  $n_1$  is a constant which depends on the nature of the solvent used to dissolve the casein, and  $a$  is a constant. It follows that when the constants are known, the concentrations of solutions containing casein can be determined with considerable accuracy by measurements of the refractive index. The change in the refractive index of a solution of an acid or base produced by the addition of a definite weight of casein is practically independent of the nature and concentration of the base or acid. The difference between the refractive index of a solution of sodium caseinate and that of water at the same temperature, is independent of the temperature between  $20^\circ$  and  $40^\circ$ .

The quantity of hydrochloric acid which just dissolves 1 gram of casein (determined by dissolving casein in sodium hydroxide, adding a known excess of hydrochloric acid, filtering, and measuring the refractive index of the solution) is about  $32 \times 10^{-5}$  gram-mols.; the alkali equivalent of 1 gram of casein, determined by a somewhat similar method, is  $11.4 \times 10^{-5}$  mols.

Solutions of bases saturated with casein are between  $10^{-5}$  and  $10^{-6}$  normal with regard to hydrogen ions. G. S.

**Production of Putrefaction Bases.** D. ACKERMANN (*Zeitsch. physiol. Chem.*, 1909, 60, 482—501).—Attempts were made to obtain pentamethylenediamine, tetramethylenediamine, and  $\delta$ -aminovaleric acid from lysine, ornithine, and arginine respectively by the action of putrefactive organisms, but without success. When, however, casein is decomposed by boiling with sulphuric acid and water, and the product freed from arginine, pentamethylenediamine is readily obtained by putrefaction, and as the amount produced depends on the amount of lysine present (an additional amount of lysine was added to the mixture), and is not affected by varying amounts of other products of the decomposition of casein, it is evident that lysine is the compound from which it is formed.

Tetramethylenediamine and  $\delta$ -aminovaleric acid are produced only when arginine is present.

Experiments on the action of putrefaction organisms on aspartic and glutamic acids, glycine, alanine, and guanidine, show that the first two acids are readily attacked, whilst glycine and alanine

were only slightly decomposed. Guanidine was partly converted into carbamide.  
N. H. J. M.

**Action of Pure Hydrogen Peroxide on Crystallised Oxy-hæmoglobin.** I. SZRETER (*Compt. rend.*, 1909, 148, 1776—1779. Compare Abstr., 1907, i, 807).—Several crystallisations are necessary to free oxyhæmoglobin from the substance which brings about catalytic decomposition of hydrogen peroxide (Senter's hæmase). A physiological solution of pure sodium sulphate is recommended instead of sodium chloride for washing oxyhæmoglobin, since this avoids the presence of chlorine in the product.  
W. O. W.

**Guanylie Acid.** PHÆBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 2469—2473. Compare Bang, Abstr., 1899, i, 179; 1901, i, 299; 1908, i, 70; Fürth and Jerusalem, Abstr., 1907, i, 993; 1908, ii, 119; Steudel, *ibid.*, 1908, i, 70; Levene and Mandel, *ibid.*, i, 587; Jones and Rowntree, *ibid.*, i, 487).—Guanylie acid appears to be similar to inosic acid (Abstr., 1908, i, 931; this vol., i, 164) in constitution. When hydrolysed by dissolving in a slight excess of sodium hydroxide solution, neutralising with acetic acid, and heating in sealed tubes at 130—135°, guanylie acid yields a guanine pentoside,  $C_{10}H_{13}O_5N_5 \cdot 2H_2O$ , analogous to inosine, and termed *guanosine*. It crystallises from water in long, silky needles resembling tyrosine. It contains no phosphorus, but gives the pentose reactions. When quickly heated, it decomposes at 237°. It dissolves in alkalis and in mineral acids, and in alkaline solution has  $[\alpha]_D^{20} - 60 \cdot 52^\circ$ . When hydrolysed with 0.1*N*-sulphuric acid it yields carnosine and guanine.

Carnosine is also formed when guanylie acid is hydrolysed by dilute mineral acid.

Whereas both inosine and guanosine are levorotatory, inosic and guanylie acids have opposite rotations.  
J. J. S.

**Yeast Nucleic Acid.** PHÆBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 2474—2478. Compare this vol., i, 447).—Guanosine (compare preceding abstract) has been isolated from the products obtained by hydrolysing the nucleic acid of yeast in neutral solution. The pentose obtained by the complete hydrolysis of the nucleic acid or of guanosine is not *l*-xylose, but *d*-ribose. The sugar termed carnosine (preceding abstract) is *d*-ribose.  
J. J. S.

**Lipoids. IV. Phosphatides of the Ox Pancreas.** SIGMUND FRÄNKEL and G. A. PARI (*Biochem. Zeitsch.*, 1909, 17, 68—77. Compare this vol., i, 276).—From the pancreas of the horse a saturated phosphatide, m. p. 167°, has been isolated; ox pancreas, however, yields a different phosphatide, now termed *vesalthin*, soluble in acetone and in methyl acetate. This phosphatide is unsaturated; it forms a cadmium compound,  $C_{32}H_{63}O_9NP \cdot CdCl_2$ , contains no galactose, and yields myristic acid,  $C_{14}H_{25}O_2$ , and an unsaturated fatty acid having fewer carbon atoms than oleic acid. It contains, further, a base which, since it yields four methyl groups attached to nitrogen, is not choline. Vesalthin is optically active, having  $[\alpha]_D + 118^\circ$  approximately.

From the alcoholic infusion of the pancreas, a compound,  
 $C_7H_{15}N, CdCl_2$ ,  
 has been obtained. This does not react with dimethylamino-  
 benzaldehyde, but shows the orcinol reaction, and may represent an  
 acetyl-pentosamine. E. F. A.

**Lipoids. V. Phosphatide of the Ox Pancreas.** SIGMUND  
 FRÄNKEL, KURT LINNERT, and G. A. PARI (*Biochem. Zeitsch.*, 1909,  
 18, 37—39).—Further proof that the base contained in vesalthin  
 (preceding abstract) is not choline is shown by the following further  
 points: the platinichloride has m. p.  $254^\circ$ , and the ratio of chlorine to  
 platinum is 5 : 1 (choline platinichloride, m. p.  $241^\circ$ , gives the ratio  
 Cl : Pt = 6 : 1). W. D. H.

**The Action of Pepsin on Egg-Albumin.** REGINALD O. HERZOG  
 and M. MARGOLIS (*Zeitsch. physiol. Chem.*, 1909, 60, 298—305). The  
 Relationship between Pepsin and Rennin. REGINALD O.  
 HERZOG (*ibid.*, 306—310).—The action of strong pepsin solutions on  
 egg-albumin follows the Schütz law; the action of rennet solutions on  
 the same protein follows the same law, but its reaction velocity is  
 slower.

Not only is there this resemblance between the two enzymes, but  
 it is pointed out that both are inhibited by the anti-pepsin of  
 Weinland obtained from the worm *Ascaris*, and their diffusion  
 coefficients are the same. If the two enzymes are not identical, they  
 exhibit great parallelism. W. D. H.

**The Maltase of Buckwheat.** R. HUERRE (*Compt. rend.*, 1909,  
 148, 1526—1528).—The dry grains of buckwheat contain a soluble  
 maltase which disappears at the commencement of germination, and  
 an insoluble enzyme which persists during this process. The maltase  
 acts between  $3^\circ$  and  $70^\circ$ , with an optimum at  $55^\circ$ . Its activity is  
 increased by partial neutralisation of the alkalinity of the medium or  
 by the addition of acetamide or amino-acids. W. O. W.

**Influence of Boric Acid on Diastatic Actions.** H. AGULHON  
 (*Compt. rend.*, 1909, 148, 1340—1342. Compare Gerber, Abstr.,  
 1908, i, 745).—Boric acid exerts as a rule a feebly retarding influence  
 on the activity of diastatic ferments. In the case of sucrase, emulsin,  
 trypsin, and pancreatic amylase, the action is slightly accelerated. The  
 diastatic coagulation of milk is favoured by the presence of boric acid.  
 W. O. W.

**Electrical Migration of Enzymes. III. Malt Diastase. IV. Pepsin.**  
 LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1909, 17, 231—234.  
 Compare this vol., i, 345).—Malt diastase was dialysed and placed as  
 middle element of the cell:

Silver in sodium chloride	Water	Ferment	Water	Copper in cupric chloride
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In neutral solution it migrates to the cathode, but a small quantity

passes to the anode. In acetic acid solution the migration is entirely cathodic; in dilute sodium carbonate solution it is entirely anodic. The undialysed ferment migrates exclusively to the cathode.

Diastase is accordingly amphoteric, as shown by adsorption experiments. Kaolin adsorbs it only in acid solution. Compared with amphoteric trypsin, diastase is more strongly positive, and shows positive properties in neutral solution; trypsin is more strongly negative, and shows positive properties only in distinctly acid solution.

*Pepsin.*—In the cell,

Silver in sodium chloride	Hydrochloric acid	Pepsin in hydrochloric acid	Hydrochloric acid	Copper in cupric chloride
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hydrogen ions travel with the current, and bring about a decrease in acidity, and so affect the behaviour of the pepsin. To get over this, the sodium chloride in the first compartment is replaced by hydrochloric acid. Under these conditions, pepsin migrates to the anode when the electric current is passed through the pure aqueous solution; it migrates to both anode and cathode in  $N/200$  and weaker acid solution, and migrates only to the cathode in  $N/50$  and  $N/40$  hydrochloric acid.

Pepsin only acts as a proteoclast in presence of a considerable proportion of acid, whereas it acts similarly to rennet only in neutral solution. It is suggested that when cathodic it acts as a proteoclast, when anodic it is the same ferment as rennet. E. F. A.

**Asymmetric Syntheses by means of Enzyme Action.**  
LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1909, 17, 257—269. Compare this vol., i, 74).—The influence of a number of foreign substances on the reaction of benzaldehyde, hydrogen cyanide, and emulsin, leading to the formation of optically active benzaldehydecyanohydrin, has been studied, in order to detect differences in the behaviour of hydrolytic and synthetic emulsin.

The addition of large quantities of alcohol does not destroy the synthetic enzyme so long as the solution is not filtered. The addition of an equal volume of alcohol to a solution of emulsin gives a filtrate which causes the formation of optically active products; if the hydrogen cyanide is added before precipitation, these have a lower rotation. This is confirmatory evidence of a compound of hydrogen cyanide with the synthetic enzyme. Liquids not miscible with water, such as chloroform, ethyl acetate, and xylene, do not prevent the synthetic action. Alkali and phenol prevent action; formaldehyde has but little influence. Half saturation with ammonium sulphate produces a precipitate; the filtrate has no synthetic action, and contains only hydrolytic enzyme; the precipitate when dissolved in water contains active synthetic enzyme. The same result is obtained on complete saturation with magnesium sulphate. In this way the hydrolytic enzyme can be obtained free from the synthetic. The unpurified enzyme acting on benzaldehyde and hydrogen cyanide produces a product of maximum optical activity in about two and a-half hours, and the optical activity subsequently decreases. The purified synthetical

enzyme gives a product, of which the optical activity is as large after two and a-half as after twenty-four hours. Pepsin and trypsin in neutral solution destroy the synthetical enzyme.

A large number of other aldehydes yield, when shaken with hydrogen cyanide and emulsin, optically active nitriles, from which in some cases optically active acids were obtained on hydrolysis. Thus acetaldehyde, isobutaldehyde, heptaldehyde, octaldehyde, citral, furfuraldehyde, *o*-methoxybenzaldehyde, anisaldehyde, cumenaldehyde, piperonal, *o*- and *m*-nitrobenzaldehydes, cinnamaldehyde, phenylacetaldehyde, phthalaldehyde, isophthalaldehyde, and terephthalaldehyde gave active products. On the other hand, from salicylaldehyde, *m*- and *p*-hydroxybenzaldehydes, *p*-nitrobenzaldehyde, protocatechu-aldehyde, methyl ethyl ketone, and hypnone, inactive products resulted. Quantitative measurements show that in all cases the emulsin accelerates the addition of hydrogen cyanide, the acceleration being very marked in the case of anisaldehyde, furfuraldehyde, and dextrose. This acceleration is observed whether or no optically active products are formed.

A full explanation for the experimentally observed facts is found in the conclusion that emulsin consists of a synthetic enzyme, bringing about the asymmetric synthesis, and a hydrolytic enzyme acting to hydrolyse the optically active nitrile.

E. F. A.

**Catalysing Constituents of Emulsin.** LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1909, 19, 186—190).—The acceleration of the addition of hydrocyanic acid to aldehydes and ketones, due to emulsin preparations, is brought about by inorganic salts contained in the latter, and especially by magnesium compounds. Acids, which reduce the degree of dissociation of the hydrogen cyanide retard the additive reaction, from which it follows that hydrogen cyanide is added in the form of ions, a result already deduced by Lapworth (*Trans.*, 1903, 83, 995) from other experiments.

G. B.

**Action of a Bulgarian Ferment on Certain Sugars.** GABRIEL BERTRAND and F. DUCHACEK (*Compt. rend.*, 1909, 148, 1338—1340; *Ann. Inst. Pasteur*, 1909, 23, 402—414).—A study of the action of the "yoghourt" ferment which occurs in curdled Bulgarian milk. This ferment has no action on arabinose, xylose, sorbose, maltose, sucrose, and mannitol, but brings about a lactic fermentation in the case of dextrose, mannose, galactose, lævulose, or lactose.

Unlike the ordinary lactic fermentation, however, the decomposition is accompanied by the production of *d*- and *l*-lactic acids in equal proportions.

W. O. W.

**The Properties and Classification of the Oxidising Enzymes, and Analogies between Enzymic Activity and the Effects of Immune Substances and Complements.** BENJAMIN MOORE and EDWARD WHITLEY (*Bio-Chem. J.*, 1909, 4, 136—167).—The authors do not consider it necessary to assume the existence of oxygenase (the peroxide-forming ferment) or catalase, and regard peroxidase as the only enzyme of this class. Traces of organic peroxides are present in

the fresh juices of most plants; they are formed from a precursor, but there is no evidence that their production is due to enzymes. These peroxides react with various compounds (for example,  $\alpha$ -naphthol, *p*-phenylenediamine, quinol, guaiacum, etc.) to produce colours, and the reaction is considerably accelerated by the enzyme peroxydase, which is widely distributed in plants. Where the organic peroxide is absent the reaction is only produced after the addition of hydrogen peroxide; it is thus possible by two tests (reagent + plant juice; reagent + hydrogen peroxide + plant juice) to discover whether both peroxide and peroxydase or peroxydase only are present. Guaiacum is less trustworthy than the other reagents, as it sometimes contains a peroxide.

An active peroxydase precipitate was analysed, and yielded C 46.8; H, 7.1; N, 10.8; O, etc., 35.3 (calculated ash-free). E. J. R.

Coaguloses. IV. D. LAWROFF (*Zeitsch. physiol. Chem.*, 1909, 60, 520—532. Compare Abstr., 1908, i, 844).—In the peptic digestion of casein two chief groups of coagulose-yielding substances are obtained: (1) of the type of proteoses with relatively little nitrogen; and (2) of the type of polypeptides; these yield hardly any bases. They yield coa-proteoses and coa-peptides respectively. The chemical individuality of these substances is still an open question. W. D. H.

Action of Different Antiseptics on the Enzymes of Yeast-Juice. FRANZ DUCHÁČEK (*Biochem. Zeitsch.*, 1909, 18, 211—227).—Small quantities of phenol (0.1%) have no deleterious action on the enzyme. Small quantities of chloroform (0.5%) and chloral hydrate (0.7%) increase the activity. The action is due to the deleterious influence of the antiseptic on the proteolytic enzyme which acts on the zymase. Benzoic and salicylic acids were found to exert, in low concentrations (0.1%), but small action on the fermentative capacity of the juice. The experiments as a whole demonstrate that the action of yeast-juice is due to the zymase, and not to any contamination with living protoplasm. The fermentation takes place in concentrations of antiseptic high enough to totally inhibit the action of any living matter. S. B. S.

Action of Yeast Enzymes. EDUARD BUCHNER and HUGO HÄHN (*Biochem. Zeitsch.*, 1909, 19, 191—218).—A discussion on the course of the action of yeast enzymes in special relationship to the work of Harden and Young and others on the co-enzyme of zymase. The loss of activity which occurs when yeast juice is kept is attributed to the action of a proteolytic enzyme (endo-tryptase) on the zymase, and the point to which special attention is directed is that the co-enzyme protects zymase from this harmful influence. The co-enzyme is particularly sensitive to the action of potassium, and the view is advanced that it is an easily saponifiable organic ester of phosphoric acid. W. D. H.

## Organic Chemistry.

Hydration of Hydrocarbons of the Acetylene Series by means of Cadmium, Zinc, and Magnesium Salts. M. G. KUTSCHEROFF (*Ber.*, 1909, 42, 2759—2762).—The author has previously shown (*Abstr.*, 1881, 883; 1884, 719) that hydrocarbons of the acetylene series can be hydrated by the agency of mercury salts. It is now found that when acetylene is heated to 100° with solutions of cadmium or zinc salts (acetate, chloride, and bromide), acetaldehyde is formed, and when the latter metal is used (as chloride or bromide), probably crotonaldehyde. *iso*Propylacetylene when heated at 150° with cadmium or zinc chlorides gives a quantitative yield of methyl propyl ketone.

J. C. C.

Glutaric Pinacone,  $\text{OH} \cdot \text{CMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CMe}_2 \cdot \text{OH}$  [ $\beta\zeta$ -Dimethylheptane- $\beta\zeta$ -diol]. PIERRE BRUYLANTS (*Bull. Acad. roy. Belg.*, 1909, 276—282).—By the action of magnesium methyl bromide on ethyl glutarate,  $\beta\zeta$ -dimethylheptane- $\beta\zeta$ -diol,  $\text{OH} \cdot \text{CMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CMe}_2 \cdot \text{OH}$ , is formed; it crystallises with a molecule of water in fine tufts, m. p. 60—61°. When heated at 140°, the hydrate loses water, giving the anhydrous pinacone, m. p. 76—77°, which re-absorbs water quite readily. Like succinic pinacone (Henry, *Abstr.*, 1906, i, 922), but much less readily, glutaric pinacone is dehydrated by dilute sulphuric acid, giving tetramethylpentamethylene oxide,  $\text{CH}_2 \langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{smallmatrix} \rangle \text{O}$ , a colourless, mobile liquid, b. p. 141—143°, with a pronounced terpene-like odour, which reacts readily with hydrochloric acid, giving a dichlorohydrin, m. p. 41—42°. The latter can also be obtained by the action of concentrated hydrochloric acid or acetyl chloride on the pinacone itself. The dichlorohydrin is decomposed slowly by cold, and very rapidly by hot, water.

Succinic pinacone (*loc. cit.*) also crystallises with water. When silky needles, m. p. 92°, of the anhydrous pinacone are moistened with a few drops of water, they are rapidly transformed into small, hard, brittle crystals of the hexahydrate, m. p. 41—42°, analogous to that of oxalic pinacone. This hydrate, however, is very unstable, losing water even by prolonged contact with a porous tile.

E. H.

Purification of Ethyl Ether. GUIDO GARBARINI (*Bull. Assoc. chim. Sucr. Dist.*, 1909, 26, 1165—1168).—The researches of Schoenbein, Babo, Hingzet, Buchner, Legler, Richardson, and Dymond have shown that ethyl ether is peroxidised when exposed to the air, and that this peroxidation is accelerated by light. A special arrangement of the receiver used in distillation to reduce the contact of the ether with air to a minimum is described. The author finds that the peroxide compound unavoidably formed is not affected by manganese dioxide, but can be completely removed by treating the ether for twenty-four hours with ferrous hydroxide. The latter is prepared in a dry

form, in order to avoid wetting the ether, in the following manner. Crystallised ferrous sulphate is powdered and mixed with a equimolecular weight of finely powdered lime. If the ferrous sulphate has not effloresced, the reaction takes place readily by virtue of its water of crystallisation, considerable heat being developed, but in some cases the addition of a small quantity of water (15—20 c.c. per 20 kilos. of mixture) is necessary. When the reaction is complete and the ferrous hydroxide commences to oxidise, the mixture is covered with lime. The crude ether is treated with this product in the proportion of 20 kilos. per 10 hectolitres. E. H.

**Dynamical Study of Two Alkyl Derivatives of Phosphoric Acid.** TH. VAN HOVE (*Bull. Acad. roy. Belg.*, 1909, 282—294).—The author has measured the electrical conductivity of, and the rate of inversion of sucrose by, diethyl hydrogen phosphate and tetrafluorodiethyl hydrogen phosphate (Swarts, this vol., i, 202). A detailed description of the purification of the two acids is given. The conductivity at 25° of tetrafluorodiethyl hydrogen phosphate varies from  $\mu_{16}$  326.9 to  $\mu_{1024}$  379.2, whilst that of diethyl hydrogen phosphate varies from  $\mu_{16}$  263 to  $\mu_{1024}$  373. From measurements of the conductivities of their sodium salts, the limiting values  $\mu_{\infty}$  382 and  $\mu_{\infty}$  379 have been deduced respectively for the two acids. The limiting conductivities give the means of determining the degree of ionisation. The latter increases from 85.57% to 99.26% in the case of tetrafluorodiethyl hydrogen phosphate when the dilution varies from 16 to 1024, and from 69.4% to 98.41% in the case of diethyl hydrogen phosphate for the same increase in dilution. With the former acid the degree of ionisation is too great at the small dilutions to allow of the calculation of the dissociation constant, but in the case of diethyl hydrogen phosphate the value 9.84 is obtained for  $K$  at dilution 16. A table is given comparing the conductivities and degrees of ionisation of the above acids with those of phosphoric acid. This indicates that the replacement of the basic hydrogen in phosphoric acid by an alkyl group enhances the acid character, whilst the more negative difluoroethyl radicle has a still greater effect. (*N*/16-Phosphoric acid solution is ionised only 32.4%.) The rates of inversion of sucrose by tetrafluorodiethyl hydrogen phosphate and diethyl hydrogen phosphate have been compared with that of dichloroacetic acid, the dissociation constant of which was found by Ostwald to be 5.14. By aid of the latter value, the degree of ionisation of dichloroacetic acid at the dilution employed (*N*/8) is found to be 0.468, and from this and the velocity constants of the sucrose inversions by the three acids, the values 0.5803 and 0.8536 are obtained for the degrees of ionisation of diethyl hydrogen phosphate and tetrafluorodiethyl hydrogen phosphate respectively at the same dilution (*N*/8). The dissociation constants are thence found to be 10.03 and 62.2 for the two acids, of which the former agrees with the value obtained by conductivity measurements. E. H.

**Decomposition of Formic Acid by Concentrated Sulphuric Acid.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1909, 15, 506—509).—The rate of evolution of carbon monoxide from solutions of different

concentrations of formic acid and of sodium formate in 90% sulphuric acid at 18° and 25° is measured. The solutions were well stirred during the measurements. The equation of the unimolecular reaction applies very well to the results; the mean values of the constants are with formic acid 0.00297 and 0.00867, with sodium formate 0.00348 and 0.00881, at 18° and 25° respectively.

T. E.

**Effect of Neutral Salts on Hydrolysis by Water.** DAVID R. KELLOGG (*J. Amer. Chem. Soc.*, 1909, 31, 886—900).—It has been shown in an earlier paper (this vol., i, 203) that the rate of hydrolysis of ethyl acetate by water is considerably affected by the addition of potassium chloride, an acceleration being produced by solutions containing from 1 to 20% of the salt, and a retardation by stronger solutions.

The investigation has now been continued, and a study made of the influence of potassium chloride, bromide, and iodide at a fixed temperature (100°) and with a fixed concentration of ethyl acetate (0.4021*N*). The concentrations of the salts have been varied from 0.1*N* to 4*N*.

The results show that the specific influence of the salts is greater in somewhat dilute solutions. As the concentration increases, the effect gradually becomes less until it reaches zero, and then becomes negative in character, so that a 4*N*-solution of potassium chloride hydrolyses the ester more slowly than does pure water. A series of curves is given showing the relations between the concentrations of the three salts and the time required by each to hydrolyse 25, 50, and 75% of the ester. The maximum accelerating power is at about 1.8*N* for potassium chloride, 0.5*N* for the bromide, and 0.25*N* for the iodide. The reactions show a distinct period of induction at the commencement, but after they have well started, the velocity is much greater than in the earlier stages, whilst towards the close of the reactions the rate decreases considerably.

Various hypotheses are suggested to explain the influence of the salts on the hydrolysis, but it is shown that none of them is capable of fully explaining all the facts of the case.

E. G.

**Catalysis of Saturated Fatty Acids.** JEAN B. SENDERENS (*Compt. rend.*, 1909, 149, 213—215. Compare this vol., i, 286).—A further study of the action of heated metallic oxides on fatty acids whereby symmetrical ketones are produced. The ketone arises from decomposition of a salt first formed by the action of the acid on the oxide. Thorium oxide is the most satisfactory catalyst, but the oxides of uranium are little inferior in this respect. Since the formation and destruction of the salt takes place with equal readiness in these cases, a good yield of the pure ketone is obtained.

With the oxides of iron, aluminium, and chromium the formation of the salt takes place less readily than its decomposition, and a good yield of ketone is only obtained when acetic acid is employed. Owing to the stability of the salts of calcium and zinc and the high temperature necessary for their decomposition, the oxides of these metals are unsuitable as catalysts. The ketone is formed in small quantity, and

is accompanied by complex pyrogenic products. The oxides of copper and cadmium behave in a similar manner, but the reaction is further complicated by reduction of the oxide to the metallic state.

W. O. W.

**Optically Active Cyanopropylisopropylacetic Acid.** EMIL FISCHER and ERICH FLATAU (*Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 876—883).—Propylisopropylacetic [isopropylvaleric] acid presents a simple case in which the magnitude of the optical activity cannot depend on the differences in the weight of the substituting groups. The racemic acid has now been carefully purified and resolved into the optically active components by means of brucine. The dextro-acid has been obtained pure; it has the high optical rotatory power  $[\alpha]_D +11.4^\circ$  in toluene. This indicates that the structural difference between the propyl and isopropyl groups is sufficient to cause a relatively marked asymmetry of the molecule; in general, isopropyl exercises in chemical changes an influence quite different from that of the propyl group.

Ethyl  $\alpha$ -cyanoisovalerate,  $C_5H_7 \cdot CH(CN) \cdot CO_2Et$  (compare Henry, *Bull. Acad. roy. Belg.*, 1889, [iii], 18, 679), is obtained as an oil by the condensation of ethyl cyanoacetate with isopropyl bromide. It has b. p. 106—109°/13 mm., 218—219° (corr.)/745 mm., and reacts further with propyl bromide and sodium, forming ethyl  $\alpha$ -cyano- $\alpha$ -isopropylvalerate,  $CN \cdot CPr^2 \cdot CO_2Et$ , a colourless oil with a bitter taste,  $D_{20}^{20} 0.943$ , b. p. 113—114°/11—12 mm., 242—243°/749 mm. (corr.). When hydrolysed with potassium hydroxide it is converted into dl-cyanoisopropylvaleric acid, b. p. 168—169.5°/13 mm. The lead salt forms minute, colourless prisms concentrically arranged; when reconverted into the acid, a thick, transparent, odourless syrup, b. p. 168—169°/13 mm., was obtained, which, on prolonged standing, solidifies to a crystalline mass, m. p. 40—48°. The acid forms soluble, crystalline calcium and barium salts and a colourless silver salt. It is more stable towards alkali than cyanoacetic acid, the presence of the two propyl groups hindering the hydrolysis of the cyano-group.

The brucine salt of d-cyanoisopropylvaleric acid crystallises in colourless, glistening, microscopic, rectangular plates, m. p. 121° (corr.), and in 10% solution in alcohol has  $\alpha -0.29^\circ$ . The corresponding acid, prepared by hydrolysis with sulphuric acid, has m. p. 94—95° (corr.) and  $[\alpha]_D^{20} +11.4^\circ (\pm 0.2^\circ)$  in toluene, whilst the value of  $\alpha$  in 10% solution in other solvents varies from  $+0.28^\circ$  in alcohol to  $+1.52^\circ$  in bromobenzene.

E. F. A.

**The Detergent Action of Soap Solutions.** WALTHER SPRING (*Bull. Acad. roy. Belg.*, 1909, 187—206).—The author criticises the theories put forward by W. S. Jevons (*Chem. Zeit.*, 1878, 2, 457), Hillger (*J. Amer. Chem. Soc.*, 1903, 25, 511), Falk (*Zeitsch. Elektrochem.*, 1904, 10, 834), and Knapp to account for the cleansing power of soap, pointing out that all of them are inadmissible as they seek only to explain the removal of fatty impurities.

When lamp-black, which has been freed from fatty impurities by prolonged exhaustion with hot benzene, is shaken with a 2% soap

solution, it is deposited almost as quickly as from pure water, whilst with soap solutions containing less than 0.5% of soap, deposition requires about ten days. From a 1% solution, however, deposition is not complete in two months, thus showing that an optimum concentration of soap exists for retaining lamp-black in suspension. Dilute acids have not, but alkalis even of the dilution of 1 in 6,000,000,000 have, greater powers of suspension than water. Methyl and ethyl alcoholic solutions of soap also exhibit optimum concentrations analogous to that of water; 0.02% and 0.005% solutions respectively having the greatest powers of suspension. When water containing lamp-black in suspension is filtered, all the lamp-black remains on the paper, but when a soap solution having lamp-black in suspension is filtered, the paper is not even blackened, thus showing that carbon forms a colloidal combination with soap and also with cellulose, the former being the more stable.

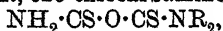
The existence of the latter colloidal combination is confirmed by the fact that the carbon is not removed from the filter-paper by washing after reversal. When the soap solution from which lamp-black has been deposited is evaporated to dryness and the residue incinerated, a greater proportion of ash is obtained than on similarly treating the soap solution to which no lamp-black has been added, thus indicating that the lamp-black causes a decomposition of the soap into an acid soap and a basic soap, and agglutinates with the former, leaving a larger proportion of basic soap in solution. Alcoholic soap solutions do not exhibit this phenomenon. The probability of carbon combining with the acid soap is strengthened by the observation that they are of opposite electrical polarity; thus when lamp-black suspended in water to which a trace of alkali has been added is submitted to electrical cataphoresis, it collects round and is deposited on the cathode, whilst a 2% soap solution on similar treatment forms a white deposit on the anode, which contains a smaller proportion of ash than that left in solution, thus indicating its acid nature. The deposit obtained from soap solutions in which lamp-black has been suspended is actually of an oily, viscous nature, quite different from the lamp-black as originally used. From the above experimental observations the conclusion is drawn that the cleansing action of soap is merely an example of substitution, and can be represented by the equation  $OD + S = DS + O$ , in which  $O$  represents the object defiled by the dirt  $D$ , and  $S$  is the soap. Both  $OD$  and  $DS$  are colloidal absorption compounds. The lack of cleansing power of alcoholic soap solutions is explained by the fact that in alcoholic solution soap is not decomposed into an acid part and a basic part.

E. H.

**Montana (Montan) and Montanin Waxes.** HUGH RYAN and THOMAS DILLON (*Sci. Proc. Roy. Dubl. Soc.*, 1909, 12, 202—208).—Irish Montana wax is found to be different from Peat wax recently described by Zaloziecki and Hausmann (*Abstr.*, 1907, i, 674), but identical with montan wax prepared from lignite by Boyen (*Abstr.*, 1902, i, 72). It is a yellow, crystalline, waxy solid having a faint odour of petroleum, m. p.  $76^{\circ}$ , acid number 73.3, saponification number 73.9, Hübl-Waller iodine number 16.0. This

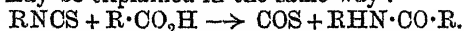
wax consists of 53% of a free acid, called by Boyen montanic acid (*loc. cit.*), and 47% of a non-saponifiable portion. Montanic acid,  $C_{28}H_{56}O_2$ , has m. p.  $83^\circ$ , acid number 131.6. The non-saponifiable portion crystallises in glistening, curved needles, m. p.  $58-59^\circ$ , and does not appear to be a saturated hydrocarbon, neither does it react with hot acetic anhydride; the Hübl-Waller iodine number is 31.13. Montanin wax has also been investigated; it is similar in chemical composition, although different in physical properties, to montana wax. It is a white, hard wax, m. p.  $95-97^\circ$ , acid number 56.9, ester number 1.0, saponification number 57.9, and contains 34.8% of non-saponifiable matter identical with that contained in montana wax, also 41.33% of montanic acid and 23.87% of sodium montanate. Irish lignite wax is found to have m. p.  $72^\circ$ , acid number 70.28; the free acid has m. p.  $80^\circ$ .  
J. V. E.

**Stability Relationships of the Anhydrides and Thioanhydrides of Organic Acids.** JULIUS VON BRAUN (*Ber.*, 1909, 42, 2743—2745).—The author points out that compounds of the general type  $E_1 \cdot C(E_2) \cdot E_2 \cdot C(E_2'') \cdot E_1'$  (compare Herzog, this vol., i, 568), where  $E_2$ ,  $E_2'$ , and  $E_2''$  denote the bivalent atoms :O and :S, and  $E_1$  and  $E_1'$  the univalent groups R, OR and  $NR_2$  ( $NH_2$  and  $NHR$ ) can be divided into two sharply-defined groups, namely, (1) the ordinary acid anhydrides,  $R \cdot CO \cdot O \cdot CO \cdot R$ , the thiocarbamino-oxides,



and the thiuram sulphides,  $NR_2 \cdot CS \cdot S \cdot CS \cdot NR_2$ , and (2) the extremely labile and characteristic yellow condensation products of dithiocarbamates with acid chlorides (and esters of chlorocarbonic acid),  $NR_2 \cdot [CS \cdot S] \cdot CO \cdot R \cdot OR$ , and the additive products of acids with isocyanic ester,  $NHR \cdot [CO \cdot O] \cdot CO \cdot R$ , which on decomposition eliminate the group shown in square brackets. The formation of acid amides by warming diphenylcarbonyl chloride with acids, and of acid esters by warming esters of chlorocarbonic acid with acids, is probably accompanied by the intermediate formation of unstable anhydrides, which readily lose carbon dioxide (shown by square brackets):  $NR_2 \cdot [CO \cdot O] \cdot CO \cdot R$ ,  $OR \cdot [CO \cdot O] \cdot CO \cdot R$ .

The well known formation of carbonyl sulphide and acid amides from thiocarbimides or thiocyanic acid and carboxylic acids at higher temperatures may be explained in the same way:



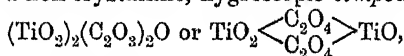
The different behaviour of the two groups is attributed to the fact that the compounds belonging to the first are symmetrical, whilst those of the second are unsymmetrical, and are, therefore, more labile.  
J. C. C.

**Additive Di-iodo-derivatives of Higher Fatty Acids of the  $C_nH_{2n-4}O_2$  Series.** ALBERT ARNAUD and SWIGEL POSTERNAK (*Compt. rend.*, 1909, 149, 220—222).—Di-iodo-derivatives of the higher members of the  $C_nH_{2n-4}O_2$  series of acids are most conveniently prepared by adding the calculated quantity of iodine to a solution of the acid in acetic acid. Tetra-iodo-derivatives cannot be prepared by a direct method. The di-iodo-derivatives are not altered by light

or by boiling with alcoholic alkali hydroxides; they are stable towards oxidising agents, but are readily reduced to the original acids. Their preparation serves as a convenient method for characterising the acids, and has been employed in isolating new members of the series from complex mixtures.

*Di-iodotariric acid*,  $\text{CH}_3 \cdot [\text{CH}_2]_{10} \cdot \text{Cl} : \text{Cl} \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$ , crystallises in slender needles, m. p.  $48.5^\circ$ ; the *ammonium* salt forms long needles, and is distinguished from the corresponding salt of di-iodoelaidic acid by its sparing solubility in alcohol. Di-iodobrassicidic acid has m. p.  $50-51^\circ$  (Liebermann and Sachse give  $47^\circ$ ). W. O. W.

**Complex Ozo-salts of Titanium.** ARRIGO MAZZUCHELLI and ENRICO PANTANELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 518-522. Compare Abstr., 1907, i, 891).—The addition of excess of hydrogen peroxide to a solution obtained by heating freshly-precipitated titanium hydroxide in less than the calculated quantity of oxalic acid results in the formation of a non-crystalline, hygroscopic compound,



which is partly hydrolysed by water.

The authors have also prepared the complex *ozolititanotartrate*,  $\text{TiO}_2 \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{C}_4\text{H}_5\text{O}_6\text{K} \cdot 10\text{H}_2\text{O}$ . T. H. P.

**Solubility of Some Comparatively Insoluble Salts of the Rare Earths.** EBERHART RIMBACH and ALWIN SCHUBERT (*Zeitsch. physikal. Chem.*, 1909, 67, 183-202).—The solubilities of the salts in question have been determined by Kohlrausch's electrical conductivity method at temperatures between  $18^\circ$  and  $26^\circ$ . The temperature-coefficient of the conductivity in the neighbourhood of  $25^\circ$  was determined in each case, and the results at  $25^\circ$  obtained by interpolation. The specific conductivity,  $\lambda$ , and the solubility,  $s$ , in mgs. per litre of the different salts at  $25^\circ$  are as follows. (1) *Oxalates* of the type  $\text{M}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ : cerium,  $\lambda = 0.651 \times 10^{-6}$ ,  $s = 0.41$ ; lanthanum,  $\lambda = 0.954 \times 10^{-6}$ ,  $s = 0.62$ ; praseodymium,  $\lambda = 1.165 \times 10^{-6}$ ,  $s = 0.74$ ; neodymium,  $\lambda = 0.765 \times 10^{-6}$ ,  $s = 0.49$ ; samarium,  $\lambda = 0.820 \times 10^{-6}$ ,  $s = 0.54$ ; ytterbium,  $\lambda = 4.853 \times 10^{-6}$ ,  $s = 3.34$ ; and yttrium with  $9\text{H}_2\text{O}$ ,  $\lambda = 1.741 \times 10^{-6}$ ,  $s = 1.00$ . (2) *Tartrates*: cerium,

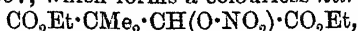
$\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ ,  $\lambda = 51.66 \times 10^{-6}$ ,  $s = 50.01$ ; lanthanum,  $\text{La}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 3\text{H}_2\text{O}$ ,  $\lambda = 58.55 \times 10^{-6}$ ,  $s = 58.80$ . (3) *Iodates*: cerium,  $\text{Ce}(\text{IO}_3)_3 \cdot 2\text{H}_2\text{O}$ ,  $\lambda = 636.8 \times 10^{-6}$ ,  $s = 1636$ ; lanthanum,  $\lambda = 692.6 \times 10^{-6}$ ,  $s = 1871$ .

In a saturated solution the oxalates are almost completely ionised; the tartrates to the extent of 89%, and the iodates to 76-77%.

G. S.

**Synthesis of Unsymmetrical Dialkylmalic Esters and Diethyl-oxalacetic Esters.** BERTHOLD RASSOW and R. BAUER (*J. pr. Chem.*, 1909, [ii], 80, 87-102. Compare Zeltner, Abstr., 1908, i, 316).—Interaction between ethyl oxalate (1 mol.), ethyl  $\alpha$ -bromoisobutyrate (1 mol.), and zinc ( $2\frac{1}{2}$  mols.) containing a little amalgamated zinc, for twenty-four hours at  $60-65^\circ$ , and treatment of the product with

water and dilute sulphuric acids, yields *ethyl aa-dimethylmalate*,  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Et}$ , b. p. 248—250° or 123—124°/12—13 mm.,  $D^{15}_D$  1.076,  $n^{21}_D$  1.4357, which forms a colourless *nitrate*,

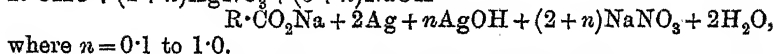
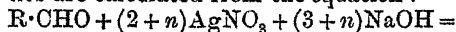


b. p. 128°/11 mm.,  $n^{22}_D$  1.4371, by treatment with concentrated nitric and sulphuric acids at 0°, and is hydrolysed by alcoholic potassium hydroxide to Baeyer and Villiger's dimethylmalic acid.

The interaction of ethyl oxalate, ethyl  $\alpha$ -bromoisobutyrate, and magnesium in ethereal solution leads to the formation of *ethyl dimethyl-oxalacetate*,  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , b. p. 230° or 115—120°/11 mm.,  $D^{15}_D$  1.05,  $n^{22}_D$  1.4313, which is hydrolysed by alcoholic potassium hydroxide to oxalic and isobutyric acids, and by warm dilute sulphuric or hydrochloric acid to isobutyrylformic acid, forms a *semicarbazone*, m. p. 95°, and by heating with phenylhydrazine, initially at 100° and finally at 190—200°, yields *ethyl 1-phenyl-4:4-dimethylpyrazolone-3-carboxylate*, m. p. 81°.

*Ethyl diethyloxalacetate*,  $\text{CO}_2\text{Et}\cdot\text{CEt}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , prepared in a similar manner from ethyl  $\alpha$ -bromo- $\alpha$ -ethylbutyrate, has b. p. 134—136°/12 mm., and forms a *phenylhydrazone*, m. p. 86°. C. S.

**Oxidation of Aldehydes by Silver Oxide.** MARCEL DELÉPINE and PIERRE BONNET (*Compt. rend.*, 1909, 149, 39—41).—When silver oxide is employed in oxidising aldehydes to acids, it is unnecessary to isolate and wash the oxide as usually recommended. The following process has been found to give almost theoretical yields of the acids in the pure state. Silver nitrate is added to an aqueous solution of the aldehyde containing sufficient alcohol to keep it in solution. A  $N/2$  or  $N/3$  solution of sodium, potassium, or preferably barium hydroxide is added at frequent intervals during two hours, with constant shaking. After twelve hours the liquid is filtered and treated with carbon dioxide. Alcohol is removed by distillation, and, if necessary, any neutral products may be removed by extraction with ether. Quantities are calculated from the equation:



This method is the only one that gives satisfactory results in the case of the polymeride of crotonaldehyde,  $\text{C}_5\text{H}_{12}\text{O}_2$ ; in this instance it is necessary to add more than  $(2+n)$  equivalents of alkali.

W. O. W.

***aa-Dialkyl- $\beta$ -keto-alcohols.*** EDMOND É. BLAISE and I. HERMAN (*Ann. Chim. Phys.*, 1909, [viii], 17, 371—398).—Mainly a recapitulation of work previously published (compare Abstr., 1904, i, 218, 219; 1905, i, 505; 1907, i, 749; 1908, i, 78, 248, 318, 596; this vol., i, 85). The following new compounds are described:  $\beta$ -Acetoxy-*aa*-dimethyl-propionyl chloride,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{COCl}$ , b. p. 84°/12 mm.; the *anilide*, white needles, m. p. 87°; and the *p*-toluidide, needles, m. p. 79°. *Ethyl hydroxy-tert-butyl ketoxime*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CET}\cdot\text{N}\cdot\text{OH}$ , small crystals, m. p. 80°; the *phenylhydrazone*, clear yellow needles, m. p. 104—105°; the *semicarbazone*, small crystals, m. p. 122°; and the

*phenylurethane*, small, colourless crystals, m. p.  $62.5^{\circ}$ . *Ethyl isopropyl ketone semicarbazone* forms needles, m. p.  $92.5^{\circ}$ .  $\alpha$ -*Methylhydraacrylic acid*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , a colourless, viscous liquid; the *ethyl ester* has b. p.  $76^{\circ}/7$  mm.; the *phenylhydrazide* forms brilliant white spangles, m. p.  $143^{\circ}$ ; the *phenylurethane*, white needles, m. p.  $122^{\circ}$ .  $\beta$ -*Acetoxyisobutyric acid*,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , b. p.  $132^{\circ}/8$  mm.; the *ethyl ester*, b. p.  $84-85^{\circ}/9$  mm.; the *chloride*, b. p.  $75^{\circ}/7$  mm.; the *anilide*, slender needles, m. p.  $100^{\circ}$ ; the  $\alpha$ -*naphthylamide*, small crystals, m. p.  $104^{\circ}$ ; the *p-toluidide*, needles, m. p.  $99^{\circ}$ .  $\beta$ -*Bromodiisopropyl ketone*,  $\text{CHMe}_2\cdot\text{CO}\cdot\text{CBrMe}_2$ , formed by the action of hydrogen bromide on isopropyl methylvinyl ketone, has b. p.  $65^{\circ}/9$  mm.; it does not give a semicarbazone.  $\beta$ -*Hydroxydiisopropyl ketone*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CHMe}_2$ , has b. p.  $80^{\circ}/10$  mm.; the *acetyl* compound has b. p.  $87^{\circ}/8$  mm.

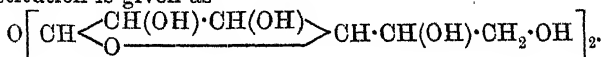
E. H.

**Colorimetric Determination of the Molecular Weights of Carbohydrates. Differentiation of Primary from Secondary and Tertiary Alcohols.** II. LEONHARD WACKER (*Ber.*, 1909, 42, 2675—2680).—The colorimetric method described previously (*Abstr.*, 1908, i, 135) has been improved by the use of stronger, 33%, sodium hydroxide whereby the coloration is rendered more durable. The molecular weights of carbohydrates are somewhat greater when dextrose is used as standard in place of maltose. The colour reaction is determined by the terminal  $\cdot\text{CHO}$  or  $\cdot\text{CH}_2\cdot\text{OH}$  group, since secondary and tertiary alcohols practically do not give a coloration with phenylhydrazinesulphonic acid. The method is being employed in the examination of starch and its degradation products. C. S.

**Synthesis of New Disaccharides of the Type of Trehalose.** EMIL FISCHER and KONRAD DELBRÜCK (*Ber.*, 1909, 42, 2776—2785).—The following method promises to be of great importance in the synthesis of disaccharides.  $\beta$ -Bromoacetodextrose and silver carbonate in dry ether are shaken with a small quantity of water so long as carbon dioxide is evolved. The precipitate contains *tetra-acetyldextrose*,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}\left\langle\begin{array}{c} \text{CH}(\text{OAc}) \\ \text{O}\cdot\text{CH}(\text{OH}) \end{array}\right\rangle\text{CH}\cdot\text{OAc}$ , m. p.  $118^{\circ}$  (corr.), whilst the ethereal filtrate leaves a viscous residue of an octa-acetyl compound. Tetra-acetyl dextrose exhibits mutarotation, an alcoholic solution (0.2521 in 4.4480 grams),  $D_{20}^{25} 0.8043$ , giving in a 1-dm. tube at  $22^{\circ}$  a rotation of  $0.10^{\circ}$  after ten minutes and  $3.77^{\circ}$  after thirty-eight hours, reduces Fehling's solution, and is easily soluble in dilute sodium hydroxide.

The octa-acetyl compound, which is obtained in better yield by repeatedly shaking silver carbonate and  $\beta$ -bromoacetodextrose in dry ether with a few drops of water, or by shaking a chloroform solution of tetra-acetyldextrose with phosphoric oxide, is separated by boiling water into two constituents, a soluble, crystalline *octa-acetylisotrehulose*,  $\text{C}_{28}\text{H}_{38}\text{O}_{19}$ , m. p.  $181^{\circ}$  (corr.), and an insoluble, amorphous substance,  $\text{C}_{28}\text{H}_{38}\text{O}_{19}$ . The latter softens at  $80^{\circ}$ , has m. p.  $115^{\circ}$ , and  $[\alpha]_{\text{D}}^{25} 31.1^{\circ}$  in benzene, scarcely affects Fehling's solution, and is probably a

mixture, which is hydrolysed by barium hydroxide to a mixture of disaccharides. Octa-acetylisotrehalose has  $[\alpha]_D^{25} - 17.2^\circ$  in benzene, does not reduce Fehling's solution, and is hydrolysed by barium hydroxide solution at the ordinary temperature to a disaccharide,  $C_{12}H_{22}O_{11}$ , an amorphous, hygroscopic powder, which does not reduce Fehling's solution, has  $[\alpha]_D^{25} - 39.4^\circ$  in aqueous solution, and yields dextrose by heating with 10% hydrochloric acid; by reason of the similarity of its properties to those of trehalose, the disaccharide is named isotrehalose. Its constitution is given as



C. S.

**Constitution of Perseulose.** GABRIEL BERTRAND (*Compt. rend.*, 1909, 149, 225—227. Compare Abstr., 1908, i, 715).—When perseulose is reduced by sodium amalgam in acid solution there is formed persitol, together with a new laevorotatory heptitol distinguished from persitol by its solubility in water and alcohol. The name *perseulitol* is proposed for this substance. The formation of two stereoisomeric sugars in this way, coupled with the fact that it resists oxidation by bromine water, indicates that perseulose is a hepta-ketose, this being the first instance of one recorded.

W. O. W.

**Two New Carbohydrates from Asparagus.** GEORGES TANRET (*Compt. rend.*, 1909, 149, 48—50).—A description of two new sugars occurring in approximately equal quantities in the roots of asparagus. The roots are boiled with water, after defecation with barium hydroxide and lead acetate, followed by treatment with sulphuric acid to remove lead, the liquid is neutralised, concentrated at a low temperature, and the sugars isolated by fractional precipitation with barium hydroxide.

*Asparagose* crystallises in spherical aggregates or in fine, microscopic needles, having the composition  $(C_6H_{10}O_5)_n \cdot H_2O$ , where  $n = 15$  or 16. It is insoluble in absolute alcohol, but soluble in two parts of cold water,  $\alpha_D - 35.1^\circ$ . On the Maquenne block it softens at  $185^\circ$ , and has m. p.  $198-200^\circ$ . Asparagose does not reduce Fehling's solution, gives no coloration with iodine, and on hydrolysis yields dextrose and laevulose. The barium compound,  $(3C_6H_{10}O_5 \cdot BaO)_n$ , is moderately soluble in water. The second carbohydrate, *ψ-asparagose*, has  $\alpha_D 30.3^\circ$ , and occurs as a white, slightly hygroscopic mass, which is much more soluble than asparagose. Like asparagose, it is hydrolysed by invertin, yielding dextrose and laevulose.

W. O. W.

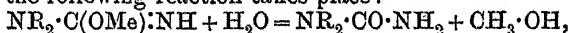
**Coloration of the Particles of Colloidal Starch and of Perfectly Soluble Starch with Iodine and Potassium Iodide.** NICOLA CASTORO (*Gazzetta*, 1909, 39, i, 603—607).—Treatment of pea-flour starch with dilute sulphuric acid yields a pseudo-solution of starch, which is precipitated in white flocks by absolute or 95% alcohol. Part of this precipitate is soluble in water; the insoluble part is coloured bluish-violet by a solution of iodine in potassium iodide, and consists of amylopectin, whilst the dissolved part, in the form of a

pseudo-solution, is coloured intensely blue, and is in part diffusible through parchment and in part colloidal. The latter consists of amylose, and is coloured a characteristic blue by iodine in potassium iodide, whilst the diffusible part is coloured a wine-violet.

These results, and others obtained with potato starch, show that the different colorations obtained depend on the magnitude of the particles, which are larger for pseudo-solutions than for true solutions of starch.

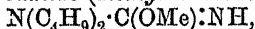
T. H. P.

**Oxygen Ethers of the Dialkylcarbamides.** RALPH H. MCKEE (*Amer. Chem. J.*, 1909, 42, 1—29).—In an earlier paper (Abstr., 1901, i, 755) some aromatic isocarbamide derivatives were described. The present paper gives an account of methyl- and ethyl-dialkylisocarbamides,  $\text{NR}_2 \cdot \text{C}(\text{OMe}) \cdot \text{NH}$ , in which R is  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_4\text{H}_9$ , or  $\text{C}_5\text{H}_{11}$ . These compounds, obtained by the action of sodium alkyl-oxides on dialkylcyanamides, are colourless oils, the densities and solubilities of which decrease as R increases from  $\text{CH}_3$  to  $\text{C}_5\text{H}_{11}$ . They are strong bases, uniting with one equivalent of the strong acids to form neutral salts, attacking the skin in the same way as potassium hydroxide, and being capable of dissolving aluminium hydroxide. When a solution of one of these bases in ether or light petroleum is treated with dry hydrogen chloride, the hydrochloride is precipitated, which, on heating, decomposes quantitatively into methyl chloride and the carbamide:  $\text{NR}_2 \cdot \text{C}(\text{OMe}) \cdot \text{NH} \cdot \text{HCl} = \text{NR}_2 \cdot \text{CO} \cdot \text{NH}_2 + \text{CH}_3\text{Cl}$ . If the bases are heated alone, they are decomposed into the cyanamide and alcohol from which they were prepared, whilst if heated in aqueous solution, the following reaction takes place:



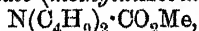
but neither ammonia nor a urethane is formed.

*Methyl diisobutylisocarbamide (methyl diisobutyliminocarbamate),*



b. p.  $102^\circ/14$  mm.,  $116^\circ/22$  mm.,  $135^\circ/42$  mm., and  $218\text{--}222^\circ$  (decomp.)/742 mm., obtained by the action of sodium methoxide on diisobutylcyanamide, has  $D_4^{20} 0.8933$ , and is soluble in 100 parts of water to the extent of 1.14 parts at  $0^\circ$ , 0.94 at  $10^\circ$ , 0.61 at  $21^\circ$ , 0.49 at  $30^\circ$ , and 0.32 at  $85^\circ$ ; the *hydrochloride* and *ferrocyanide* are described. *Diisobutylcarbamide*,  $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NH}_2$ , b. p.  $180^\circ/25$  mm., m. p.  $72\text{--}74^\circ$ , may be prepared by the action of potassium isocyanate on diisobutylamine hydrochloride; its *oxalate*, m. p.  $115^\circ$  (decomp.), and *picrate*, m. p.  $90\text{--}91^\circ$ , are described. *Benzoylmethyl diisobutylisocarbamide*,  $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{C}(\text{OMe}) \cdot \text{NBz}$ , forms a viscid oil, and, when heated with dilute hydrochloric acid at  $100^\circ$ , is converted into methyl chloride and benzoyl diisobutylcarbamide; the *hydrochloride* decomposes rapidly at the ordinary temperature with formation of the same products. *Benzoyl diisobutylcarbamide*,  $\text{N}(\text{C}_4\text{H}_9)_2 \cdot \text{CO} \cdot \text{NHBz}$ , m. p.  $123\text{--}123.5^\circ$ , crystallises in stout, rhombic plates.

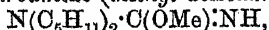
*Methyl diisobutylcarbamate (methyl diisobutylurethane),*



b. p.  $204^\circ/753$  mm., obtained by the action of methyl chlorocarbonate on diisobutylamine in presence of potassium hydroxide, has a characteristic odour, and is soluble at  $18^\circ$  in 4000 parts of water, 1200 parts

of 3*N*-hydrochloric acid, or 200 parts of 12*N*-hydrochloric acid. The corresponding *ethyl* ester, b. p. 100°/13 mm. and 203°/757 mm., is soluble at 17° in 1600 parts of water, 640 parts of 3*N*-hydrochloric acid, or 320 parts of 12*N*-hydrochloric acid.

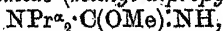
*Methyl diisocarbamide* (*methyl diisoamyliminocarbamate*),



b. p. 125°/7 mm., 133°/12 mm., and 153°/30 mm., has  $D_{15}^{20}$  0.8860, and is soluble in 1500 parts of water at 15°; the *hydrochloride* melts at 104° (decomp.). *Diisocarbamide*,  $\text{N}(\text{C}_5\text{H}_{11})_2 \cdot \text{CO} \cdot \text{NH}_2$ , was obtained as an oil; its *oxalate*, m. p. 102.5° (decomp.), and *picrate* are described.

*Ethyl diisocarbamide* (*ethyl diisoamyliminocarbamate*) has b. p. 158°/28 mm.; its aqueous solution blackens mercurous chloride, and gives a white precipitate with solution of mercuric chloride. The *hydrochloride* has m. p. 125° (decomp.).

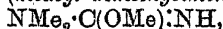
*Methyldipropylisocarbamide* (*methyl dipropyliminocarbamate*),



behaves with mercury salts in the same way as *ethyl diisocarbamide*; its *hydrochloride* decomposes at the ordinary temperature. *Methyl dipropylcarbamate* (*methyldipropylurethane*),  $\text{NPr}_2 \cdot \text{CO}_2\text{Me}$ , b. p. 191°/751 mm., is soluble at 18° in 300 parts of water or 160 parts of 3*N*-hydrochloric acid. *Ethyl dipropylcarbamate* boils at about 200°/749 mm.

*Ethyldipropylisocarbamide* (*ethyl dipropyliminocarbamate*), b. p. 92°/10 mm., does not decompose at 100°.

*Trimethylisocarbamide* (*methyl dimethyliminocarbamate*),



b. p. 60.5°/27 mm., 86°/98 mm., and 146.5° (decomp.)/755 mm., is readily volatile with the vapour of ether or alcohol, and is completely miscible with all solvents; its salts are deliquescent, and undergo rapid decomposition at the ordinary temperature. A slightly impure specimen had  $D_{15}^{20}$  0.9708. This compound dissolves silver oxide and aluminium hydroxide, but not cupric hydroxide. It gives a black precipitate with mercurous nitrate and a white precipitate with mercuric chloride. The *hydrochloride* melts at 91° (decomp.).

Pinner has shown that imino-ethers decompose slowly at the ordinary temperature, and more quickly on heating, into the nitrile and alcohol from which they were prepared. An analogous decomposition has now been observed with some of the isocarbamides. Thus when trimethylisocarbamide is heated at 100° in a sealed tube, it decomposes into dimethylcyanamide and methyl alcohol. Under similar conditions, ethylisocarbamide yields ethyl alcohol and melamine, together with small quantities of dicyanodiamide.

E. G.

**Guanidine Perchromate.** KARL A. HOFMANN and KARL BUCHNER (*Ber.*, 1909, 42, 2773—2776).—When guanidine carbonate, water, and chromium trioxide are warmed at 30—35° to expel carbon dioxide, and then treated at 0° with 33% hydrogen peroxide, a precipitate of *guanidine perchromate*,  $(\text{CN}_2\text{H}_5)_2\text{CrO}_5 \cdot \text{H}_2\text{O}$ , is obtained. It forms small, brownish-yellow, double-refracting prisms, yields 7 equivalents of oxygen with 2% sodium hydroxide, 13 equivalents

with alkaline potassium permanganate, 9 equivalents with 15% sulphuric acid, 12 equivalents with acidified potassium permanganate, forms the usual blue solution with ether and dilute sulphuric acid, and is decomposed by boiling water, forming guanidine chromate. Since the *potassium* salt,  $K_3CrO_8$ , is obtained by treatment with 15% potassium chloride at a low temperature, guanidine perchromate is a true salt and not a metal ammonia. C. S.

**New Method of Preparing Ammonium Thiocyanate and Thiocarbamide.** GIUSEPPE INGILLERI (*Gazzetta*, 1909, 39, i, 634—639).—When 6 grams of carbon disulphide and 8 grams of ammonium carbonate are heated together in a sealed tube at 100—110°, they react, giving ammonium dithiocarbamate, thus:  $CS_2 + NH_4 \cdot O \cdot CO \cdot O \cdot NH_4 = H_2O + CO_2 + NH_2 \cdot CS \cdot S \cdot NH_4$ . If, however, the temperature is kept at 120—130°, ammonium thiocyanate is formed:  $NH_2 \cdot CS \cdot S \cdot NH_4 = H_2S + NH_4 \cdot NCS$ , whilst at 160° a quantitative yield of thiocarbamide is obtained.

The interaction of carbon disulphide and ammonium carbonate in presence of alcohol at the ordinary pressure gives a quantitative yield of ammonium thiocyanate, whilst at 160° in a sealed tube these compounds give a product having the same m. p. as diethylthiocarbamide. T. H. P.

**Reaction between Ferric Compounds and Thiocyanates.** CORRADO BONGIOVANNI (*Boll. Chim. Farm.*, 1909, 48, 483—485).—Reply to Brioni's criticisms (this vol., i, 92) on the author's work on this subject (*Abstr.*, 1908, i, 770, 859). T. H. P.

**Hexathiocyno-salts of Molybdenum.** JOHANNA MAAS and JULIUS SAND (*Ber.*, 1909, 42, 2642—2646. Compare *Abstr.*, 1908, i, 397, 513, 961; Rosenheim and Garfunkel, *ibid.*, i, 614; Rosenheim, this vol., i, 558).—The potassium and ammonium salts have not similar compositions, as stated by Rosenheim, but are to be represented by the formulæ  $K_3Mo(SCN)_6 \cdot H_2O, 4H_2O$  and  $(NH_4)_3Mo(SCN)_6 \cdot H_2O, 3H_2O$ .

The corresponding acetates are strictly isomorphous, and have the analogous formulæ  $K_3Mo(SCN)_6 \cdot H_2O, HOAc$  and  $(NH_4)_3Mo(SCN)_6 \cdot H_2O, HOAc$ .

The thiocyanate can be determined accurately in the case of the complex molybdenum salts, although not with complex thiocyanochromium compounds. J. J. S.

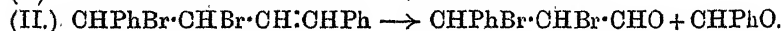
**Prussian Blue and Turnbull's Blue.** KARL A. HOFMANN (*J. pr. Chem.*, 1909, ii, 80, 150—152).—In reply to Müller and Stanisch (this vol., i, 142), the author reaffirms his opinion that soluble Prussian blue and soluble Turnbull's blue are identical. They have the composition  $KFe'''[Fe(CN)_6]_x \cdot 2H_2O$ , and behave alike optically and towards water, ammonium hydroxide, oxalic acid, ammonium oxalate, and ammonium tartrate. C. S.

**New Method of Preparing Nitrosobenzene.** BERNARDO ODDO (*Gazzetta*, 1909, 39, i, 659—661).—Nitrosobenzene may be prepared

in 56% yield by the action of nitrosyl chloride on magnesium phenyl bromide:  $\text{MgPhBr} + \text{NOCl} = \text{MgBrCl} + \text{Ph}\cdot\text{NO}$ . T. H. P.

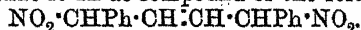
**Course of the Addition of Bromine to Conjugated Ethylene Linkings.** FRITZ STRAUS (*Ber.*, 1909, 42, 2866—2885).—With the object of testing the accuracy of Thiele's theory that in the formation of a bromine additive compound of a substance containing the conjugated ethylene linking, the bromine atoms attach themselves in the  $\alpha\delta$ -position, the author has studied the action of ozone on the bromine additive compound of *s*-diphenylbutadiene,  
 $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh}$ .

A substance of the formula (I) should on oxidation with ozone break at the double linking to give two molecules of bromophenylacetaldehyde, whereas a substance of the constitution (II) should give a mixture of dibromocinnamaldehyde with benzaldehyde:



The latter reaction was found to take place on passing a current of ozone through a solution of the dibromide in carbon tetrachloride solution, and it follows from this that the bromine atoms were added in the 1:2-position, and not in the  $\alpha\delta$ -position as required by the theory. The dibromocinnamaldehyde was identified by conversion into the crystalline monobromo-derivative or into  $\beta$ -bromostyrene, whilst the benzaldehyde was identified in the form of benzoic acid.

Similarly, by subjecting the dibromo-additive compound of monophenylbutadiene,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2$ , to the action of ozone, the author obtained a mixture of benzaldehyde with a brominated aliphatic aldehyde, which, however, could not be identified. Since these substances must have been produced by the oxidation of a compound of the constitution  $\text{CHPh}\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , it follows that the bromine atoms were added in the  $\gamma\delta$ -position. The addition of hydrogen to both mono- and di-phenylbutadiene, however, takes place in accordance with Thiele's theory in the  $\alpha\delta$ -position, and when butadiene itself is exposed to the action of bromine, both the  $\alpha\delta$ - and the  $\alpha\beta$ -dibromides are produced; it has further been shown by Wieland that the additive compound formed from diphenylbutadiene and nitrogen peroxide is an  $\alpha\delta$ -compound of the formula



The similarity in action which is thus seen to subsist between hydrogen and nitrogen peroxide as opposed to bromine may be explained by assuming that hydrogen is added on in the atomic form, and that the nitrogen peroxide when dissolved in organic solvents acts as a simple molecule, and, accordingly, in both cases the substance to be added is present in the form in which it is to be added on, whereas in the case of bromine the addition is molecular. P. H.

**Cyanobenzylamines.** OTTO FISCHER and H. WOLTER (*J. pr. Chem.*, 1909, [ii], 80, 102—112).—During unsuccessful attempts to prepare *o*-cyanobenzaldehyde, the following new compounds have been

obtained. *o*-Cyanobenzylaniline does not form a nitroso-derivative. *p*-Cyanobenzylaniline,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NHPh}$ , m. p.  $86^\circ$ , obtained from aniline and *p*-cyanobenzyl chloride at  $90^\circ$ , forms a *hydrochloride*,  $\text{C}_{14}\text{H}_{12}\text{N}_2\cdot\text{HCl}$ , m. p.  $215^\circ$  (decomp.), and a *nitroso-derivative*,  $\text{C}_{14}\text{H}_{11}\text{ON}_2$ , m. p.  $90^\circ$ , and is oxidised in acetone by aqueous potassium permanganate to *p*-cyanobenzanilide,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NHPh}$ , m. p.  $178-179^\circ$ . *Di-p*-cyanobenzylaniline,  $\text{C}_{22}\text{H}_{17}\text{N}_3$ , m. p.  $181-182^\circ$ , is a by-product in the preparation of *p*-cyanobenzylaniline. *m*-Cyanobenzylaniline, m. p.  $70^\circ$ , is prepared in a similar manner to the para-isomeride, and forms a *hydrochloride*, *picrate*, m. p.  $158^\circ$ , and *nitrosoamine*, m. p.  $63^\circ$ . *o*-Cyanobenzylmethylamine, m. p.  $100-105^\circ$ , prepared from *o*-cyanobenzyl chloride and 33.5% methylamine, forms a *hydrochloride*,  $\text{C}_9\text{H}_{10}\text{N}_2\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ , and an *aurichloride*, but not a nitrosoamine. *o*-Cyanobenzyltrimethyl-*p*-phenylenediamine,  $\text{C}_{16}\text{H}_{17}\text{N}_3$ , m. p.  $135^\circ$ , forms a *hydrochloride*,  $\text{C}_{16}\text{H}_{17}\text{N}_3\cdot\text{HCl}\cdot 3\text{H}_2\text{O}$ , an orange-red *picrate*, darkening at  $185^\circ$  and decomposing at  $200^\circ$ , and with nitrous acid a red nitro-compound,  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_4$ , m. p.  $139^\circ$ .

*p*-Cyanobenzyltrimethyl-*p*-phenylenediamine, m. p.  $183^\circ$ , forms a yellow *nitrosoamine*,  $\text{C}_{16}\text{H}_{16}\text{ON}_4$ , m. p.  $105-106^\circ$ , which is converted by dilute sulphuric acid into *p*-cyanobenzaldehyde. C. S.

**Constituents of Coal Tar. Ethylbenzene.** GUSTAV SCHULTZ and A. SANDER (*Ber.*, 1909, 42, 2633-2636. Compare Noelting and Palmar, *Abstr.*, 1891, 1197).—Dinitroethylbenzene (Weisweiler, *Abstr.*, 1900, i, 291) has b. p.  $163^\circ/10$  mm.,  $167.8^\circ/13$  mm.,  $178.5^\circ/18$  mm.,  $187^\circ/24.5$  mm., and  $195.5^\circ/33$  mm., and when reduced with ammonium sulphide yields 2-nitro-4-amino-1-ethylbenzene,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{Et}\cdot\text{NH}_2$ , which crystallises from light petroleum in orange-yellow prisms, m. p.  $43-44^\circ$ . The *acetyl* derivative,  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2$ , forms yellowish-brown crystals, m. p.  $100-101^\circ$ .

Trinitroethylbenzene (Weisweiler, *loc. cit.*) yields coloured additive compounds with arylamines and aromatic hydrocarbons.

With aniline it yields light red prisms, m. p.  $45^\circ$ ; with *p*-toluidine, blood-red needles, m. p.  $25^\circ$ . The corresponding compound of trinitrotoluene and *p*-toluidine has m. p.  $69-70^\circ$ .

Trinitroethylbenzene and *o*-toluidine yield blood-red prisms, m. p.  $35^\circ$ . With monomethylaniline the nitro-compound yields red prisms, m. p.  $44^\circ$ ; with *m*-4-xylidine, red prisms, m. p.  $52^\circ$ ; with benzidine, black prisms, m. p.  $73^\circ$ ; with *o*-tolidine, violet-black prisms, m. p.  $85^\circ$ ; with  $\alpha$ -naphthylamine, wine-red plates, m. p.  $72-73^\circ$ ; with  $\beta$ -naphthylamine, purplish-red needles, m. p.  $61-63^\circ$ , and with naphthalene, yellow prisms, m. p.  $58^\circ$ . All these compounds contain 1 molecule of nitro-compound united with 1 molecule of amine or hydrocarbon, and they are all comparatively unstable (compare *Trans.*, 1901, 79, 522; 1903, 83, 1334).

When reduced with ammonium sulphide, the trinitro-compound yields *s*-dinitroaminoethylbenzene,  $\text{C}_8\text{H}_9\text{O}_4\text{N}_3$ , which crystallises from light petroleum in lemon-yellow prisms, m. p.  $110^\circ$ . J. J. S.

**Abnormal Salts. II.** ANTONI KORCZYŃSKI (*Bull. Acad. sci. Cracow*, 1909, 610-627. Compare *Abstr.*, 1908, i, 977).—It has been

shown previously that the tendency of substituted phenols to form abnormal ammonium salts at the ordinary temperature or at  $0^{\circ}$  to  $-17^{\circ}$  is conditioned by the presence and the position of certain atoms or groups in the acidic substance, and that substituents in the di-ortho-positions exert the greatest influence. The investigation has been extended to include fifty-eight substituted phenols, cresols, naphthols, benzoic and cinnamic acids, the substituents being nitro-groups and halogens, with the following results. In nitrophenols and nitrobenzoic acids the tendency to abnormal salt formation is greatest when the nitro-group is in the para-position, but in nitrocinnamic acids when the substituent is in the ortho-position, and so also in monohaloid benzoic acids. In dinitrophenols the tendency is greatest in the 2:6-compound, but in halogen disubstituted cresols, abnormal salt formation is most marked when the halogen atoms are in the *o:p*-positions with respect to the hydroxyl group. The fact that 2:4-dinitro-1-naphthol absorbs 1 mol.  $\text{NH}_3$ , whilst 1:6-dinitro-2-naphthol absorbs 2, is explicable by Kaufler's stereo-formula of naphthalene, according to which positions 1 and 6 are di-ortho with respect to position 2. When a halogen atom in 2:4:6-trihalogenphenols is replaced by a nitro-group, the tendency is, or is not, diminished according as the nitro-group is in the ortho- or the para-position to the hydroxyl group. When a nitro-group in 2:4:6-trinitrophenol is replaced by a halogen atom, the tendency is not diminished when the halogen is in the ortho-position, and in the para-position only when the halogen atom is iodine.

It is remarkable that the addition of ammonia to nitrophenols is most favoured when the nitro-group is in that position in which it most hinders the addition of hydrogen chloride to the corresponding nitro-aniline.

C. S.

**The Oxidation of Phenol. The Effect of Some Forms of Light and of Active Oxygen on Phenol and Anisole.** HARRY D. GIBBS (*Philippine J. Sci.*, 1909, 4, 133—151. Compare this vol., i, 221, and Kohn and Freyer, *J. Soc. Chem. Ind.*, 1893, 12, 111).—Pure phenol remains colourless in sunlight when in contact with the indifferent gases, hydrogen, nitrogen, and carbon dioxide, but is coloured in the presence of oxygen. In the dark, the rate is not appreciable at the ordinary temperature, but increases with rise of temperature. It can be measured at  $100^{\circ}$ , and at the boiling point of phenol is fairly rapid. In sunlight the rate of coloration is rapid, and increases directly with the temperature. The coloration is due to oxidation, and the principal products formed are quinol, *p*-benzoquinone, and catechol, together with some carbon dioxide. The coloration itself is probably due to the formation of quinone condensation products, of which the red compound, phenoquinone, is one.

Ozone reacts readily with phenol, yielding quinol, *p*-benzoquinone, catechol, glyoxylic acid, and carbon dioxide. An ozonide was not isolated. Anodic oxygen also reacts readily with phenol, yielding *p*-benzoquinone. The experiments lead to the conclusion that the activity is not due to oxygen gaseous ions.

The nature of the glass through which the sunlight passes has an

influence on the rate of the reaction. Glasses which absorb ultra-violet rays most completely have the greatest retarding effect.

Ozone could not be detected in pure dry oxygen sealed in a glass tube and exposed to sunlight. The altitude of the sun, the thickness of the atmosphere through which it passes, and the atmospheric conditions influence the rate of coloration.

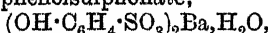
Anisole is not coloured by oxygen or ozone in the presence of sunlight.

The reactivity of phenol is augmented by the absorbed wave-lengths at about  $\lambda$  291 to  $\lambda$  243.

The purest phenol can only be obtained by distillation in an atmosphere free from oxygen. J. J. S.

**Phenolsulphonic Acid Method for the Estimation of Nitrates in Water.** I. Composition of the Reagent and of the Reaction Product. EMIL M. CHAMOT and D. S. PRATT (*J. Amer. Chem. Soc.*, 1909, 31, 922—928).—A study of the standard phenolsulphonic acid employed for the estimation of nitrates in water has shown that it contains phenol-2:4-disulphonic acid, together with small quantities of *p*-phenolsulphonic acid, and that the yellow coloration produced in the reaction is not due to picric acid, as is generally supposed, but to an alkali nitrophenol-sulphonate.

An investigation has been made of the barium salts of the phenol-sulphonic acids, and the observations of Obermiller (*Abstr.*, 1907, i, 910) on barium *o*-phenolsulphonate and phenol-2:4-disulphonate are confirmed. Barium *p*-phenolsulphonate,



forms rosettes of slender, white, silky needles. It is shown that mixtures of the phenolsulphonic acids can be analysed micro-chemically by means of these salts, the crystalline forms of which are depicted by micro-photographs.

When *o*-phenolsulphonic acid is added to nitrates and afterwards diluted and rendered alkaline, a dark green solution is obtained without any yellow tint. *p*-Phenolsulphonic acid does not react with nitrates in the cold, but on heating it behaves in the same way as the ortho-acid. Phenol-2:4-disulphonic acid reacts to form pure yellow solutions. If the mono-acids are submitted to prolonged heating with the nitrate, greenish-yellow solutions are produced, owing to the conversion of some of the mono-acid into the di-acid.

A bibliography of the subject is appended.

E. G.

**Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane.** ADOLF VON BAEYER (*Ber.*, 1909, 42, 2624—2633).—Phenol crystals turn brown immediately when brought into contact with triphenylmethyl chloride. When gently warmed, a deep brown solution is obtained; when this is heated more strongly, the colour disappears, but is restored on cooling.

The reaction between the two compounds is accompanied by the evolution of hydrogen chloride. It has not been found possible to isolate a definite additive compound from the brown solution, as the

addition of diluents immediately destroys the colour. The addition of water produces hydrogen chloride and triphenylcarbinol, or, if the mixture has stood for some time, hydroxytetraphenylmethane (Abstr., 1902, i, 769). The coloration is not due to the presence of hydroxytetraphenylmethane or to *α*-phenoxytriphenylmethane. The latter compound,  $\text{CPh}_3\cdot\text{OPh}$ , prepared by the action of triphenylmethyl chloride on potassium phenoxide, crystallises from a mixture of ether and light petroleum in six-sided plates or prisms, m. p.  $103^\circ$ . This ether is stable towards alkalis, but is immediately hydrolysed by acids.

The following phenols produce intense brown colorations with triphenylmethyl chloride: phenol, *m*- and *p*-cresols, *p*- and *o*-chlorophenols, *p*-nitrophenol, quinol, and its monomethyl ether, resorcinol and its monomethyl ether, catechol, pyrogallol, ethyl *p*-hydroxybenzoate, *p*-hydroxybenzaldehyde,  $\alpha$ - and  $\beta$ -naphthol. With *o*-cresol and 1:3:4-xenol it is necessary to use a large amount of chloride in order to produce an intense coloration, and *o*-nitrophenol, picric acid, trichlorophenol, thymol, guaiacol, ethyl salicylate, and salicylaldehyde do not give a coloration. Some of the latter, however, give a brown coloration with the chloride in the presence of a little stannic chloride.

Tri-*p*-chloro- and tri-*p*-bromo-phenylmethyl chlorides dissolve in phenol to brown solutions, whereas the corresponding iodo-derivative gives a reddish-violet coloration. Tri-*o*-anisylmethyl chloride gives a blue coloration with phenol or guaiacol. The additive compounds, which are undoubtedly formed, do not appear to be quinonoid compounds, as suggested by Gomberg.

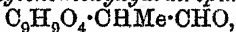
*Hydroxymethoxytetraphenylmethane*,  $\text{CPh}_3\cdot\text{C}_6\text{H}_5(\text{OH})\cdot\text{OMe}$ , prepared by the action of triphenylmethyl chloride on guaiacol in the presence of stannic chloride, crystallises in colourless needles or prisms, m. p.  $220^\circ$ .

It is suggested that in triphenylmethyl the free linking of the carbon atom unites with the centric valencies of the benzene rings, thus destroying the symmetry of these rings and producing colour.

J. J. S.

**Presence of 5:6-Dimethoxy-3:4-methylenedioxy-1-allylbenzene in Oil of Samphire.** MARCEL DELÉPINE (*Compt. rend.*, 1909, 149, 215—217.\* Compare Borde, *Bull. Sci. pharm.*, 1909, 16, 132).—The portion of the oil of samphire (*Crithmum maritimum*) boiling above  $200^\circ$  at ordinary pressure has been separated into two fractions: (1) a dextrorotatory fraction, b. p.  $90\text{--}95^\circ/13\text{ mm.}$ , constituting 5% of the original oil; (ii) an optically inactive fraction, b. p.  $157\text{--}158^\circ/13\text{ mm.}$ ,  $D_4^{20} 1.1753$ , which constitutes 40% of the oil and has been identified with 5:6-dimethoxy-3:4-methylenedioxy-1-allylbenzene (Thoms, Abstr., 1904, i, 742).

Oxidation of *isopiole* with mercuric oxide and iodine furnishes 5:6-dimethoxy-3:4-methylenedioxyhydratropaldehyde,

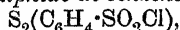


b. p.  $189^\circ/17\text{ mm.}$ ,  $D_4^{20} 1.2567$ ,  $n_D^{25} 1.53191$ ; its *oxime* has m. p.  $102^\circ$ ; the *semicarbazone* has m. p.  $148^\circ$ . Oxidation of the aldehyde leads

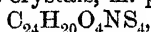
\* and *Bull. Soc. chim.*, 1909, [iv], 5, 926—930.

to the formation of the corresponding acid,  $C_{12}H_{14}O_6$ , m. p.  $119^\circ$ , and 5:6-dimethoxy-3:4-methylenedioxyacetophenone,  $C_9H_9O_4 \cdot COMe$ , m. p.  $88-89^\circ$ , which can be further oxidised to the ketonic acid,  $C_9H_9O_4 \cdot CO \cdot CO_2H$ . W. O. W.

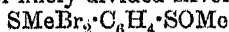
**Dithioquinol.** THEODOR ZINCKE and W. FROHNEBERG (*Ber.*, 1909, 42, 2721—2736).—The authors have prepared a number of derivatives of dithioquinol. 4:4'-Disulphido-di-benzenesulphonyl chloride,



prepared by treating the corresponding potassium salt with phosphoryl chloride, forms large, square crystals, m. p.  $142^\circ$ ; the dianilide,

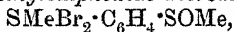


crystallises in white needles, m. p.  $189-190^\circ$ . On reduction with zinc dust and hydrochloric acid in alcoholic solution, the dichloride yields dithioquinol,  $SH \cdot C_6H_4 \cdot SH$ ; the diacetyl derivative,  $C_{10}H_{10}O_2S_2$ , of which crystallises in white tablets, m. p.  $126^\circ$ . Oxidising agents convert dithioquinol into a yellow, amorphous sulphide,  $(C_6H_4S_2)_n$ , which is also the first product of the action of chlorine or bromine. On chlorination, dithioquinol is converted into benzene-1:4-disulphonyl chloride, m. p.  $138^\circ$  (Körner and Monselise, this Journ., 1877, i, 81, give  $131^\circ$ ). Benzene-1:4-disulphonamide forms colourless tablets, m. p.  $248^\circ$ . Bromination of dithioquinol leads to the formation of benzene-1:4-disulphonyl bromide,  $C_6H_4(SO_2Br)_2$ , colourless needles, m. p.  $148^\circ$ . 1:4-Dimethylthiolbenzene,  $C_6H_4(SMe)_2$ , prepared by methylating dithioquinol, best with methyl sulphate, crystallises in colourless, pearly leaflets, m. p.  $85^\circ$ , and has a characteristic odour. On oxidation with nitric acid, or by treating the tetrabromide (see below) with dilute alkali, phenylene 1:4-dimethyldisulphoxide,  $C_6H_4(SOMe)_2$ , is formed; this crystallises in large, colourless, rhombic tablets or stumpy needles, m. p.  $188^\circ$ , and with mercuric chloride gives a characteristic compound,  $C_6H_4(SOMe)_2 \cdot HgCl_2$ , crystallising in white needles, m. p.  $220^\circ$ . On oxidising the disulphoxide with nitric and hydrochloric acids, it is converted into phenylene-1:4-dimethyldisulphone,  $C_6H_4(SO_2Me)_2$ , which crystallises in colourless, rhombic tablets, m. p.  $258-260^\circ$ . 1-Methylthiolphenyl 4-methylsulphoxide,  $SMe \cdot C_6H_4 \cdot SOMe$ , prepared by the action of finely divided silver on the dibromide,



(see below), crystallises in long, colourless needles, m. p.  $102^\circ$ ; with mercuric chloride it gives a compound crystallising in long needles. 1:4-Dimethylthiolbenzene tetrabromide,  $C_6H_4(SMeBr_2)_2$ , prepared either by the action of hydrogen bromide on phenylene 1:4-dimethyldisulphoxide or by the addition of bromine to 1:4-dimethylthiolbenzene, forms dark red needles, m. p.  $87-90^\circ$  (decomp.); the compound occurs in two modifications, the second being obtained by recrystallising the dark red needles just described from carefully dried chloroform, and forming thick tablets or columns, m. p.  $107-109^\circ$  (decomp.), which are almost black in reflected, and dark garnet-red in transmitted, light. On exposure to moist air, the tetrabromide decomposes into hydrogen bromide and the disulphoxide; when the solution is evaporated in a vacuum, however, the tetrabromide is regenerated. With mercuric chloride the compound,  $C_6H_4(SOMe)_2 \cdot HgBr_2$ , large needles, m. p.  $225^\circ$ ,

is obtained. On treating the tetrabromide with 33% alkali, bromine is removed and 1:4-dimethylthiolbenzene is formed. By the action of sodium methoxide and methyl alcohol on the tetrabromide, the chief product is 1:4-dimethylthiolbenzene, some 1-methylthiolphenyl 4-methylsulphoxide is also formed, and on one occasion a substance crystallising in stout, rhombic tablets, m. p. 148°, was obtained. *1-Methylthiolphenyl 4-methylsulphoxide dibromide*,



prepared by passing hydrogen bromide into a chloroform solution of phenylene 1:4-dimethyldisulphoxide, forms yellow needles, m. p. 74° (decomp.). *1:4-Dimethylthiolbenzene tetraiodide*,  $\text{C}_6\text{H}_4(\text{SMeI}_2)_2$ , is prepared by treating the disulphoxide with concentrated hydriodic acid or by the addition of iodine to 1:4-dimethylthiolbenzene. It crystallises in long, almost black needles, m. p. 82–89° (decomp.). In distinction from the tetrabromide it is very stable, but the iodine is readily eliminated by the usual agents. When mixed with glacial acetic acid and subjected to the action of a stream of chlorine, it dissolves, and iodine trichloride and benzene-1:4-disulphonyl chloride are formed; when chlorinated in presence of chloroform, however, a yellow, crystalline compound,  $\text{C}_6\text{H}_{10}\text{O}_2\text{Cl}_6\text{I}_2\text{S}_2$ , is produced, which, in presence of methyl alcohol, yields phenylene 1:4-dimethylsulphone. *1:4-Dibromo-2:5-dimethylthiolbenzene*,  $\text{C}_6\text{H}_2\text{Br}_2(\text{SMe})_2$ , prepared by heating a mixture of dimethylthiolbenzene, bromine, and glacial acetic acid, crystallises in colourless needles, m. p. 198°. On treatment with zinc dust and hydrochloric acid in glacial acetic acid solution, dimethylthiolbenzene is regenerated, and the dibromo-compound forms an additive compound with bromine, which crystallises in long, dark red needles, m. p. 80–90° (decomp.). The dibromo-compound also yields an additive compound with iodine, which on treatment with chlorine furnishes dibromobenzenedisulphonyl chloride. *1:4-Di-trichloromethylthiolbenzene*,  $\text{CCl}_3 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CCl}_3$ , prepared by chlorinating the corresponding dimethylthiolbenzene in chloroform solution, crystallises in white needles, m. p. 148°; on reduction with zinc dust in glacial acetic acid solution, it yields dithioquinol and dimethyl sulphide; with alcoholic potash it gives dithioquinol, and, on warming with aniline, dithioquinol and triphenylguanidine are produced. *Phenylene 1:4-di-trichloromethylsulphoxide*,  $\text{CCl}_3 \cdot \text{SO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO} \cdot \text{CCl}_3$ , prepared by chlorinating the disulphoxide or by oxidising 1:4-di-trichloromethylthiolbenzene with hydrogen peroxide in glacial acetic acid solution, crystallises in colourless tablets or leaflets, m. p. 192°; on reduction with zinc dust in acetic acid solution, dimethyl sulphide is produced. J. C. C.

**Addition of Dimethyl Sulphate to Thiophenol Ethers.** KARL AUWERS and F. ARNDT (*Ber.*, 1909, 42, 2713–2715).—In the interaction between *p*-methylthioltoluene and dimethyl sulphate (this vol., i, 175) a by-product is always obtained, which has now been found to be the additive product, *p*-tolyl dimethylsulphonium methyl sulphate,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{SMe}_2 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OMe}$ . It is readily prepared by warming equimolecular quantities of its components on the water-bath. It crystallises in glistening leaflets, m. p. 97°. The compound dissociates on distillation, and is decomposed on heating with alkalis. When

*p*-ethylthioltoluene is substituted for the methyl compound in this reaction, *p*-tolylmethylethylsulphonium methyl sulphate, a colourless, odourless, viscid oil, solidifying at a low temperature to a transparent, glassy mass, is produced. On heating alone or with soda-lime, it decomposes into *p*-methylthioltoluene and methyl ethyl sulphate. In this way it is possible to convert the ethyl ether of a thiophenol into the corresponding methyl ether. No similar additive products are obtained when diethyl sulphide or methyl iodide are used instead of dimethyl sulphate.

J. C. C.

**A Reaction of Aromatic Inner Anhydrides and Anhydride-forming Compounds.** BRUNO BARDACH (*Zeitsch. anal. Chem.*, 1909, 48, 438—448).—The reaction of proteins recently described (Abstr., 1908, ii, 332) has been more fully investigated, and it is found that the thin, yellow needles which are obtained as precipitate in place of iodoform, although they have not yet been obtained perfectly pure, contain 91.78% iodine, and have m. p. about 141—143° (decomp.). In the presence of internal aromatic anhydrides, or substances which under given conditions form anhydrides, iodine and potassium iodide in alkaline acetone solution do not yield iodoform, but a similar yellow, crystalline iodine compound. From numerous experiments the conclusion is drawn that aromatic hydroxy-acids containing long side-chains in positions favourable to anhydride formation, also polyhydroxy-ketones, form anhydrides under the conditions of this test. It is found possible by using this test to ascertain directly whether an aromatic substance forms an anhydride.

J. V. E.

**New Method of Ester Formation by the Action of Chlorocarbonic Esters on Acids.** ALFRED EINHORN (*Ber.*, 1909, 42, 2772—2773).—Herzog's claim (this vol., i, 568) is not original, since the author has already shown (this vol., i, 568) that esters and anhydrides of benzoic and *p*-nitrobenzoic acids are obtained by the action of ethyl chlorocarbonate on the two acids.

C. S.

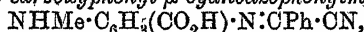
**Aromatic Nitroso-compounds, Azomethinecarboxylic Acids, and the Preparation of Benzoquinoneoximecarboxylic Acid.** JOSEF HOUBEN, WALTER BRASSERT, and LEO ETINGER (*Ber.*, 1909, 42, 2745—2759).—5-Nitroso-*N*-methylantranilic acid (Houben and Brassert, Abstr., 1908, i, 27), in aqueous alkaline solution, apparently undergoes intramolecular change, thus:  $\text{NO}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{NHMe} \rightarrow \text{NOH}\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{NMe}$ . Confirmation of this is afforded by the fact that, in anhydrous solvents, such as sodium alkyloxides, the acid condenses quantitatively with compounds containing an "acidic" methylene group, whilst in aqueous alkaline solution only a small yield is obtained. It is possible, also, to condense the ester of the acid, in presence of sodium alkyloxide, to azomethine compounds without hydrolysis taking place. Dyes analogous to those of the phenazine series are also produced by condensing the acid or its ester with aniline hydrochloride,  $\beta$ -phenylnaphthylamine,  $\beta$ -ethylnaphthylamine, diphenyl-*m*-phenylenediamine, ditolylnaphthylenediamine, tolylenediamine, etc., in glacial acetic acid solution in the presence of hydrogen chloride. On

treatment with magnesium or zinc in ammonium chloride solution, the acid is first decolorised, and is then gradually transformed into an intensely blue dye. The authors have also discovered that *p*-benzoquinoneoximecarboxylic acid can readily be prepared in good yield by treating nitrosomethylanthranilic acid with cold dilute alkali hydroxide for a short time.

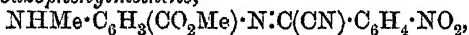
The acid can be condensed with various agents in a similar manner to nitrosomethylanthranilic acid.

5-Nitroso-*N*-methylanthranilic acid is readily prepared by treating a hydrochloric acid solution of methylanthranilic acid with sodium nitrite; the *methyl* ester crystallises in small, bright green needles, *m. p.* 119° (corr.), and the *ethyl* ester forms small, grass-green needles, *m. p.* 87—88°.

5-Nitroso-*N*-ethylanthranilic acid,  $\text{NO} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{NH}\text{Et}$ , prepared by the action of a cold alcoholic solution of hydrogen chloride on *o*-ethylnitrosoaminebenzoic acid, or by treating ethylanthranilic acid with concentrated hydrochloric acid and sodium nitrite, crystallises in bright green, rectangular, prismatic rods, *m. p.* 152° (decomp.). The condensation of 5-nitroso-*N*-methylanthranilic acid with phenylacetonitrile in the presence of sodium ethoxide leads to the production of 4-methylamino-3-carboxyphenyl- $\mu$ -cyanoazophenylmethine,



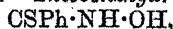
which is a yellowish-red dye, *m. p.* 223—224°; the sodium salt forms red needles. 4'-Nitro-4-methylamino-3-carboxyphenyl- $\mu$ -cyanoazophenylmethine, similarly obtained from the nitroso-acid and *p*-nitrophenylacetonitrile, crystallises in dark red needles, *m. p.* 260°; the sodium salt is dark red. Ethyl 4-methylamino-3-carboxyphenyl- $\mu$ -cyanoazomethine-carboxylate,  $\text{NHMe} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{N} : \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , prepared by condensing 5-nitrosomethylanthranilic acid and ethyl cyanoacetate, is a red substance, *m. p.* 203—204°. 4'-Nitro-4-methylamino-3-carbomethoxyphenyl- $\mu$ -cyanoazophenylmethine,



prepared by condensing methyl 5-nitrosomethylanthranilate with *p*-nitrophenylacetonitrile, crystallises in reddish-brown needles with a blue reflex, *m. p.* 200—201°; it forms a colourless salt with concentrated sulphuric acid. Reduction of 5-nitrosomethylanthranilic acid in ammoniacal solution with ammonium chloride and magnesium furnishes a blue dye resembling indigotin, which probably has the constitution  $\text{NHMe} \cdot \text{C}_6\text{H}_2(\text{CO}_2\text{H})(\text{NH}_2) \cdot \text{N} : \text{C}_6\text{H}_3(\text{CO}_2\text{H}) : \text{NMe}$ .

[With ERICH KELLNER.]—*p*-Benzoquinoneoximecarboxylic acid may readily be prepared by the action of cold concentrated sodium hydroxide on 5-nitrosomethylanthranilic acid. When condensed with *p*-nitrophenylacetonitrile it yields 4'-nitro-4-hydroxy-3-carboxyphenyl- $\mu$ -cyanoazophenylmethine,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{CO}_2\text{H}) \cdot \text{N} : \text{C}(\text{CN}) \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , forming dull yellow crystals, *m. p.* 231—236°. J. C. C.

Thiohydroxamic Acids. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 687—690).—Thiobenzhydroxamic acid,



prepared by the action of hydroxylamine on dithiobenzoic acid:  $\text{Ph} \cdot \text{CS}_2\text{H} + \text{NH}_2 \cdot \text{OH} = \text{CSPH} \cdot \text{NH} \cdot \text{OH} + \text{H}_2\text{S}$ , is very unstable,

decomposing mostly according to the equation:  $\text{CPh}\cdot\text{NH}\cdot\text{OH} = \text{Ph}\cdot\text{CN} + \text{S} + \text{H}_2\text{O}$ . Its solution gives with ferric chloride a violet-blue coloration, or with excess, a black precipitate. Its *benzyl* ester,  $\text{OH}\cdot\text{N}\cdot\text{CPh}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ , m. p. 120—122°, yields a *benzoyl* derivative,  $\text{OBz}\cdot\text{N}\cdot\text{CPh}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ , separating from alcohol in crystals, m. p. 135°. Its *dibenzoyl* derivative,  $\text{OBz}\cdot\text{N}\cdot\text{CPh}\cdot\text{SBz}$ , crystallises from alcohol in small, colourless prisms, m. p. 90—92°. This dibenzoyl compound, like that of  $\beta$ -benzhydroxamic acid, is not hydrolysed by dilute hydrochloric acid, but is decomposed by alcoholic potassium hydroxide, partly with formation of thiobenzhydroxamic and benzoic acids:  $\text{NOBz}\cdot\text{CPh}\cdot\text{SBz} + 2\text{H}_2\text{O} = \text{OH}\cdot\text{N}\cdot\text{CPh}\cdot\text{SH} + 2\text{Ph}\cdot\text{CO}_2\text{H}$ , and partly into benzhydroxamic, thiobenzoic, and benzoic acids:  $\text{OBz}\cdot\text{N}\cdot\text{CPh}\cdot\text{SBz} + 2\text{H}_2\text{O} = \text{OH}\cdot\text{N}\cdot\text{CPh}\cdot\text{OH} + \text{Ph}\cdot\text{CO}\cdot\text{SH} + \text{Ph}\cdot\text{CO}_2\text{H}$ . T. H. P.

**Saponification of Phenylisonitroacetonitrile to the Amide by means of Hydrogen Peroxide.** A. J. VAN PESKI, jun. (*Ber.*, 1909, 42, 2763—2764).—When sodium phenylisonitroacetonitrile is treated with hydrogen peroxide in presence of sodium hydroxide, *sodium phenylisonitroacetamide*,  $\text{NO}_2\text{Na}\cdot\text{CPh}\cdot\text{CO}\cdot\text{NH}_2$ , is formed; it separates on evaporation of its alcoholic solution in a vacuum in small, white rods. With bromine it yields  *$\alpha$ -bromonitrophenylacetamide*,  $\text{NO}_2\cdot\text{CBrPh}\cdot\text{CO}\cdot\text{NH}_2$ , which crystallises in small, white needles, m. p. 113°, and when heated above its m. p. decomposes into bromine, nitric oxide, and phenylglyoxylamide. J. C. C.

**Cinnamic Acids of Different Origin.** EMIL ERLÉNMEYER [with OTTO HERZ and G. HILGENDORFF] (*Ber.*, 1909, 42, 2649—2655. Compare this vol., i, 156).—Small amounts of hetero- $\beta$ -cinnamic acid appear to be present in storax-cinnamic acids obtained from different natural sources. The presence of this acid was shown by fractionating the ester carefully and hydrolysing the residue, when either synthetic cinnamic or hetero-cinnamic acid is obtained. Control experiments proved that the storax ester is not transformed into the hetero-ester when heated.

The cinnamic acid obtained from styryl methyl ketone is a mixture of the storax and hetero-acids. Benzylidenemalononic acid appears to exist in two forms, one of which yields storax acid by the loss of carbon dioxide, and the other, under similar conditions, the hetero-acid.

The acid obtained by Perkin's synthesis and also by Claisen's condensation (*Abstr.*, 1890, 891) is a mixture of the storax and hetero-acids (synthetical cinnamic acid).

When phenylpropionic acid is reduced, some 50% of storax-cinnamic acid is obtained; the remainder of the propionic acid undergoes decomposition, yielding phenylacetylene. The propionic acid prepared from storax-cinnamic acid gives a much better yield of storax acid when reduced. The phenylpropionic acid, prepared from the hetero- $\beta$ -acid, has m. p. 138°, and when reduced yields the hetero-acid or mixtures of the hetero- and storax acids. J. J. S.

Differences in the Cinnamic Acids due to the Synthetical Materials Used. EMIL ERLÉNMEYER [with OTTO HERZ and G. HILGENDORFF] (*Ber.*, 1909, 42, 2655—2675. Compare preceding abstract).—Ordinary benzaldehyde contains two constituents, the more volatile of these yields storax-cinnamic acid by Perkin's synthesis, and the less volatile, hetero- $\beta$ -cinnamic acid. The separation of the two constituents can be accomplished by repeated fractionation.

Natural benzaldehyde, which contains hydrogen cyanide, yields as chief condensation product storax acid, whereas the same aldehyde when freed from hydrogen cyanide yields synthetical cinnamic acid.

When hetero-cinnamic acid is oxidised to benzaldehyde and this is then condensed with sodium acetate and acetic anhydride, the product formed is the hetero-acid.

When heated with acetic anhydride the synthetical acid is converted into the storax acid or its anhydride, and a similar conversion occurs when the synthetical acid or the hetero- $\beta$ -acid is sublimed.

The storax acid is stable towards alkalis or acetic anhydride, but when its solution in cold concentrated sulphuric acid is kept for some five weeks and then poured into water, it is partly transformed into hetero- $\beta$ -acid or hetero- $\alpha$ -acid. If the benzaldehyde, obtained by oxidising the storax acid with warm permanganate whilst steam is blown through, is subjected to Perkin's synthesis, the product is synthetical cinnamic acid.

Storax acid can be obtained from ordinary synthetical benzaldehyde by Perkin's synthesis provided copper or copper acetate is present. The aldehyde recovered in the ordinary Perkin's synthesis also yields pure storax acid when condensed again with acetic anhydride and sodium acetate.

Crystallographic measurements of the dibromides from storax-, synthetical-, and hetero-cinnamic acids indicate that the dibromides from the storax- and hetero-acids are distinct, and that the dibromide of the synthetical acid is not homogeneous.

[With K. BUBE].—Determinations of the affinity constants of storax- $\alpha$ -, storax- $\beta$ -, hetero- $\alpha$ -, and hetero- $\beta$ -acids indicate that all four acids have much the same value;  $K = 0.0036—0.0040$ . The acids do not appear to yield saturated solutions at 25° even when left in contact with water for several days and shaken.

J. J. S.

3:5-Dinitro-4-hydroxybenzoic Acid. HEINRICH SALKOWSKI (*Annalen*, 1909, 367, 348—353).—The author has repeated and confirmed Reverdin's work (*Abstr.*, 1908, i, 537). It is shown that the potassium salt,  $\text{OK} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CO}_2\text{K}$ , crystallises with  $2\frac{1}{2}\text{H}_2\text{O}$  in yellow needles, with  $2\text{H}_2\text{O}$  in red plates (compare this *Journal*, 1872, 555), and with  $1\frac{1}{2}\text{H}_2\text{O}$  in orange-red needles. The last two pass into the stable hydrate with  $2\frac{1}{2}\text{H}_2\text{O}$  when kept in contact with the solution at the ordinary temperature.

W. H. G.

Crystallographic Study of *o*-Thymotic Acid and of Two Isomeric Thymotides. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 534—537).—The author gives crystallographic data of

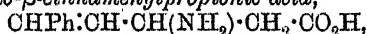
the following compounds, prepared by Spallino and to be described shortly.

*o*-Thymotic acid,  $C_{11}H_{12}O_3$ , m. p.  $129^\circ$ , crystallises from light petroleum in prisms belonging to the monoclinic system:  $a:b:c = 1.0724:1:0.9039$ ,  $\beta = 93^\circ 24'$ .

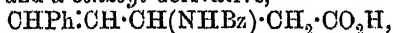
The thymotide,  $C_{22}H_{24}O_4$ , m. p.  $174^\circ$ , crystallises from benzene in hexagonal prisms belonging to the rhombohedral system:  $a:c = 1:1.1092$ ,  $\alpha = 94^\circ 11'$ .

The thymotide,  $C_{22}H_{24}O_4$ , m. p.  $209^\circ$ , crystallises in a biaxial system.  
T. H. P.

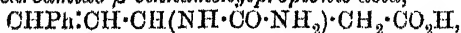
Unsaturated Compounds. VII. Addition of Hydroxylamine to Unsaturated Acids containing Conjugate Double Linkings. THEODOR POSNER and KARL RÖHDE (*Ber.*, 1909, 42, 2785—2794. Compare this vol., i, 583).—Riedel and Schulz's work (this vol., i, 581), which encroaches on that of the authors', had already been done by them; it contains two errors. The compound obtained by the action of free hydroxylamine on the ester of cinnamenylacrylic acid in the cold is  $\beta$ -hydroxylamino- $\beta$ -cinnamenylpropionylhydroxamate,  $CHPh:CH:CH(NH \cdot OH) \cdot CH_2 \cdot C(OH)(NH \cdot OH)_2$ , and not hydroxylamine  $\beta$ -hydroxylamino- $\beta$ -cinnamenylpropionylhydroxamate. Riedel and Schulz are incorrect in stating that hydroxylamine and cinnamenylacrylic acid only react to form an unstable hydroxylamine salt, for when the two substances are heated in methyl alcohol for 240 hours,  $\beta$ -amino- $\beta$ -cinnamenylpropionic acid,



m. p.  $238^\circ$  (decomp.), is formed. The acid, which is obtained after thirty hours' heating when methyl cinnamenylacrylate is used in place of the acid itself, forms a silver salt, a hydrochloride,  $C_{11}H_{13}O_2N \cdot HCl$ , m. p.  $195$ — $196^\circ$ , and a benzoyl derivative,



m. p.  $205^\circ$ , the methyl ester of which,  $C_{19}H_{19}O_3N$ , has m. p.  $142$ — $145^\circ$ .  $\beta$ -Amino- $\beta$ -cinnamenylpropionic acid and potassium cyanate in hot water yield  $\beta$ -carbamido- $\beta$ -cinnamenylpropionic acid,



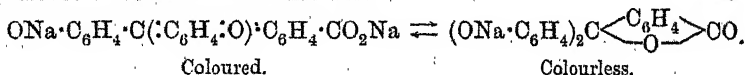
m. p.  $187^\circ$  (decomp.), which on heating forms cinnamenylidihydroureacil,  $NH \begin{smallmatrix} \diagup CO \cdot CH_2 \\ \diagdown CO \cdot NH \end{smallmatrix} > CH:CH:CHPh$ , m. p.  $231.5$ — $232.5^\circ$ . This fact and the formation of benzoic acid by the oxidation of  $\beta$ -benzoylamino- $\beta$ -cinnamenylpropionic acid by cold alkaline potassium permanganate are proofs that hydroxylamine is added on at the  $\alpha\beta$ -position in cinnamenylacrylic acid.  
C. S.

Hofmann's Reaction. V. Action of Sodium Hypochlorite and a Little Alkali on Phthalimide. ERNST MOHR, FR. KÖHLER, and H. ULRICH (*J. pr. Chem.*, 1909, [ii], 80, 1—33. Compare this vol., i, 420).—The authors have continued the series of experiments which show that in the Hofmann reaction slight variations in the quantity of alkali, in the temperature, or in the method of mixing may materially affect the yield and even the nature of the product. The present paper deals with the claim (D.R.-P. 127138) that sodium

hypochlorite and phthalimide in the absence of free alkali yield, not anthranilic acid, but isatoic acid. This result, unexpected in view of the instability of carbamic acids towards acids, is confirmed by the authors. When equal molecular quantities of phthalimide and 2*N*-sodium hydroxide are treated rapidly at 7–8° with an equal molecular quantity of sodium hypochlorite, free from alkali, the temperature rises to 40–45°, and the solution turns dark brown. When a sample, tested every ten seconds, does not liberate iodine from acidified potassium iodide, the solution is poured into hydrochloric or acetic acid at 0°, whereby a precipitate of isatoic anhydride is obtained. When the same solutions, with or without a small excess of sodium hydroxide, are mixed so slowly at –5 to –10° that the final temperature does not exceed 2°, and then kept for six to eight hours at 0°, four crystalline fractions are obtained, the first being almost pure isatoic anhydride and the last, sodium anthranoylanthranilate. Finally, when a solution of sodium hypochlorite containing a small excess of sodium hydroxide, at 14°, is added slowly to a solution of equal molecular quantities of phthalimide and 2*N*-sodium hydroxide at –3°, the final temperature is 45–50°; the mixture is warmed until carbon dioxide ceases to be evolved, and then cooled, whereby a precipitate of sodium anthranoylanthranilate is obtained. This is the best method of obtaining the substance; the *potassium*, *barium*, and *copper* salts are described.

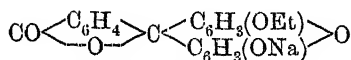
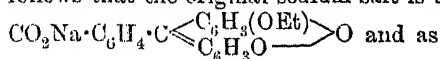
C. S.

**Theory of Indicators and Reactions of Phthaleins and their Salts.** SALOMON F. ACREE and E. A. SLAGLE (*Amer. Chem. J.*, 1909, 42, 115–147. Compare *Abstr.*, 1908, i, 423, 653).—The authors show briefly the inadequacy of the quinone theory, of Baeyer's theory of halochromy, and of Ostwald's theory of electrolytic dissociation, to explain the colour phenomena of phenolphthalein and its salts. Stieglitz's view that the red salts of phenolphthalein are carboxylic and not phenolic is opposed by Meyer and Spengler's proof that the coloured salts are dibasic salts. The theory that the chief cause of the colour of the salts of aurin, phenolphthalein, etc., is not a quinonoid but a quinonephenol group,  $\text{OK} \cdot \text{C}_6\text{H}_4 \cdot \text{C} : \text{C}_6\text{H}_4 \cdot \text{O}$ , proposed by Acree and adopted by many investigators, is explained at length and supported by numerous illustrations. The same theory explains the behaviour of the salts of phenolphthalein and fluorescein on alkylation; both the colour phenomena and the alkylation reactions point to the presence of tautomeric dibasic salts:

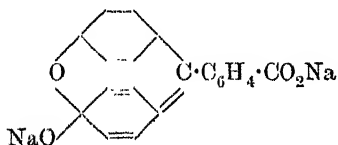


The presence of such tautomeric salts in the case of fluorescein is shown as follows. The *sodium* salt,  $\text{CO}_2\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_3(\text{OEt}) \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_3\text{O} \end{array} \text{O}$ , is obtained by treating a solution of sodium hydroxide with an excess of fluorescein ethyl ether and evaporating the filtrate after extracting it with carbon tetrachloride. The salt is much less coloured than that of fluorescein, and by treatment with alcoholic ethyl iodide yields a mixture of the colourless fluorescein diethyl ether and the coloured fluorescein

diethyl ester-ether. Since it is proved experimentally that these two are not interconvertible under the conditions of their formation, it follows that the original sodium salt is tautomeric, reacting as



The authors incline to the view that the ultimate cause of the colour of the salts of phenolphthalein, etc., is a third tautomeric salt of the annexed constitution, formed by intramolecular rearrangement between

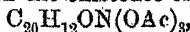


the CO of the quinone group and the phenolic  $\cdot\text{ONa}$ . Salts of analogous constitution have been obtained by Acree in the triazole series, and assumed by Hantzsch in the salts of nitrophenols, *p*-hydroxybenzaldehyde, and *p*-hydroxybenzophenone. The chief reason for believing that such an intramolecular salt is the cause of the colour of the salts of phenolphthalein is the work of Jackson and others, who have shown that in non-aqueous solution, quinones and sodium phenoxide, sodium  $\beta$ -naphthoxide, or dimethylaniline yield intensely coloured additive double salts. It has indeed been shown that benzoquinone or anthraquinone yields deeply coloured compounds with salts of *o*-cresol, *p*-cresol, phenol, quinol, pyrogallol, resorcinol, or dimethylaniline, the colours being destroyed by the addition of acid.

The latter part of the paper deals with the solubility of phenolphthalin, tetrabromophenolphthalin, *p*-hydroxydiphenylphthalide, and their derivatives in dilute sodium hydroxide. Experiments to determine the affinity constants of these weak acids by Koelichen's dilatometric method show that the catalytic influence of the hydroxyl ions of the alkali on a 10% solution of diacetone alcohol is materially diminished by the presence of the salt of the weak acid. A new metallic dilatometer is described, with which very concordant results are obtained.

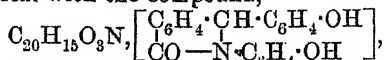
C. S.

**Phthaleinoximes.** RICHARD MEYER and S. M. KISSIN (*Ber.*, 1909, 42, 2825—2838).—The authors attempt to settle the constitutions of the oximes of phenolphthalein and quinolphthalein, and propose formulæ which harmonise with the properties of the oximes, but, it is admitted, present one or two difficulties. Friedländer's original quinonoid formula of phenolphthaleinoxime has been abandoned, and the lactonoid formula,  $\text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2 \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{N}(\text{OH}) \end{array} \text{CO}$ , does not account for the colour of the oxime, or for its ready hydrolysis, since the similarly constituted anilides are stable to hydrolysing agents. The formula  $\text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2 \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{O} \end{array} \text{C} \cdot \text{N} \cdot \text{OH}$  contains the chromophore,  $\cdot\text{C} \cdot \text{N} \cdot$ , and harmonises with the existence of a triacetate,



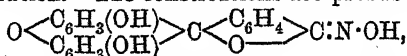
m. p. 229—230°, and tribenzoate, m. p. 175°, but presents the following difficulty.

Friedländer reduced the yellow oxime to a colourless substance,  $C_{20}H_{17}O_3N$ , identical with the compound,



synthesised by H. Meyer from hydroxyphenylphthalide and *p*-aminophenol; the authors have confirmed the composition  $C_{20}H_{15}O_3N$  for the substance obtained by both methods, but cannot state during which preparation the intramolecular change has taken place, which must have occurred if the preceding formula of phenolphthaleinoxime is correct.

Of the three oximes of quinolphthalein, the  $\alpha$ -isomeride has almost certainly the constitution  $O < \begin{array}{c} C_6H_3(OH) \\ C_6H_3(OH) \end{array} > C < \begin{array}{c} C_6H_4 \\ N(OH) \end{array} > CO$ , since it is colourless, forms a *trimethyl ether*, m. p. 123—124°, a *triacetate*, m. p. 210°, and a *tribenzoate*, m. p. 226—227°, and, like the analogously-constituted phthaleinanilides, is not attacked by zinc and sodium hydroxide. The yellowish-brown  $\beta$ - and  $\gamma$ -quinolphthaleinoximes are probably stereoisomerides, the  $\gamma$ -oxime, being the stable form, having the anti-configuration. The constitutions are probably



since the  $\gamma$ -oxime forms a *tribenzoate*, m. p. 275—280°, and the  $\beta$ -isomeride yields by treatment with zinc and sodium hydroxide a reduction product which re-oxidises to the  $\gamma$ -oxime. This reduction, however, presents a difficulty, since the similarly-constituted phenolphthaleinoxime suffers reduction in a different manner.

Although hydroxylamine does not, as a rule, attack lactones and similarly constituted compounds, there seems to be little doubt that such a reaction occurs with the phthaleins (possibly by reason of their solubility in alkalis), since hydroxyphenylphthalide forms an *oxime* (colourless leaflets containing 1 mol. MeOH from methyl alcohol), m. p. 215—216° (*dibenzoate*, m. p. 233—234°), and hydroxydiphenylphthalide also forms an *oxime*, m. p. 204—205°, which separates from ether in colourless, and from alcohol in yellow, crystals, and forms a *dibenzoate*, m. p. 150—151°. The aliphatic lactone of  $\alpha$ -hydroxy- $\alpha$ -methylglutaric acid, which is also soluble in alkali hydroxides, does not yield an oxime. C. S.

**New Preparation of spiroCyclanes.** DON RADULESCU (*Ber.*, 1909, 42, 2770—2772).—When equal molecular quantities of ethyl succinate and ethyl cyclopropane-1:1-dicarboxylate in ether at 0° are treated with sodamide, the product, decomposed by cold water, yields the spirocycloane derivative,  $\begin{array}{c} CH_2 \\ CH_2 \end{array} > C < \begin{array}{c} CO \cdot CH \cdot CO_2Et \\ CO \cdot CH \cdot CO_2Et \end{array}$ , m. p. 151—152° (decomp.). The substance and that from ethyl cyclobutandicarboxylate are being investigated. C. S.

**Behaviour of *N*-Alkylaldoximes towards Iodine and the Condition of Iodine in Solutions.** ERNST BECKMANN [and, in part, M. EBERT, HANS NIESCHER, and E. SCHULZ] (*Annalen*, 1909, 367, 271—303).—This investigation was commenced with the object of

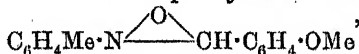
ascertaining whether *N*-alkylaldoximes, like oximino-compounds, are converted into their isomerides by the action of iodine. It is found, however, that when treated with iodine in an indifferent solvent, such as benzene, they at first yield soluble, simple iodine additive products, but subsequently hydrogen periodides separate, which, as a rule, consist of 2 mols. of the *N*-ether combined with 1 mol. of hydrogen iodide and 1 mol. of iodine, less frequently with 1 mol. of hydrogen iodide and 2 mols. of iodine. Sunlight and heat accelerate the formation of the hydrogen periodides, probably because they induce the production of hydrogen iodide at the cost of part of the *N*-ether.

The compounds containing 3 atoms of iodine in the mol. are generally yellow, brown, or red, whilst those with a higher proportion of iodine are green to steel-blue. The iodine is only loosely bound, and the compounds are dissociated in solution to a more or less degree depending on the temperature, likewise on the nature and quantity of the solvent. Aqueous solutions of sulphites and thiosulphates decompose the hydrogen periodides with elimination of hydrogen iodide and iodine and regeneration of the *N*-ether.

The latter part of the paper is devoted to a discussion of the work of various investigators relative to the state of iodine in solutions. The accumulated evidence supports the author's view that in brown solutions of iodine most of the halogen is combined with the solvent, whilst in violet solutions the greater part of it exists in an uncombined state.

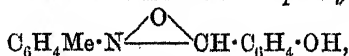
*Bis-N-phenylbenzaldoxime hydrogen tri-iodide*,  $2C_{13}H_{11}ON, HI_3$ , is a brownish-red substance, m. p. 101—102°; the *N-p-tolyl* compound,  $2C_{14}H_{13}ON, HI_3$ , is yellowish-red, and has m. p. 137—138°; the isomeric *N-o-tolyl* compound crystallises in small, slender, yellowish-red needles, m. p. 93—94°, whilst the *N-m-tolyl* derivative forms small, golden-green, felted needles, m. p. 85—86°; the analogous *N-benzyl* compound,  $2C_{14}H_{13}ON, HI_3$ , forms reddish-brown crystals, m. p. 108—109°.

*N-Phenyl-p-anisaldoxime* yields a *hydrogen penta-iodide*,  $2C_{14}H_{13}O_2N, HI_5$ , green crystals, m. p. 110—111°, and a *hydrogen tri-iodide*,  $2C_{14}H_{13}O_2N, HI_3$ , red crystals, m. p. 133—134°. *N-p-Tolylanisaldoxime*,



crystallises in white needles, m. p. 128—129°; the *hydrogen tri-iodide* forms yellowish-red needles, m. p. 121—122°. *Bis-N-o-tolylanisaldoxime hydrogen tri-iodide*,  $2C_{15}H_{15}O_2N, HI_3$ , m. p. 115—116°, is reddish-violet; the *hydrogen penta-iodide* is green, m. p. 102—103°. *N-m-Tolylanisaldoxime*,  $C_{15}H_{15}O_2N$ , crystallises in white needles, m. p. 88—89°; the *hydrogen tri-iodide* forms yellowish-green needles, m. p. 120—121°. *Bis-N-benzylanisaldoxime hydrogen tri-iodide*,  $2C_{15}H_{15}O_2N, HI_3$ , crystallises in orange-yellow needles, m. p. 174—175°.

Hydrogen periodides of the *N*-phenyl, *N-m-tolyl*, and *N-benzyl* ethers of salicylaldoxime could not be isolated. *N-p-Tolylsalicylaldoxime*,



forms golden-yellow crystals, m. p. 112—113°; the *hydrogen penta-*

iodide forms very dark green needles, m. p. 156—157°. *N*-*o*-Tolyl-salicylaldoxime crystallises in small, yellow needles, m. p. 99—100°; the *hydrogen tri-iodide* crystallises in small, dark green, felted needles, m. p. 167—168°.

*N*-Phenyl-*o*-nitrobenzaldoxime,  $C_{13}H_{10}O_3N_2$ , m. p. 94°, and *N*-*p*-tolyl-*o*-nitrobenzaldoxime,  $C_{14}H_{12}O_3N_2$ , colourless needles, m. p. 113—114°, do not yield crystalline hydrogen periodides. *N*-Benzyl-*o*-nitrobenzaldoxime yields the *hydrogen periodides*:  $2C_{14}H_{12}O_3N_2 \cdot HI_3$ , a red substance, m. p. 113—114°;  $2C_{14}H_{12}O_3N_2 \cdot HI_5$ , compact, steel-blue crystals, m. p. 81—82°;  $3C_{14}H_{12}O_3N_2 \cdot HI_5$ , compact, golden-green crystals, m. p. 94—95°.

When hydrogen iodide is passed into a solution of *N*-phenyl-anisaldoxime, a pale yellow precipitate of the *hydriodide*,  $C_{14}H_{13}O_2N \cdot HI$ , is obtained; the addition of more hydrogen iodide results in the formation of a *periodide* (41.1% iodine), crystallising in golden-green needles, m. p. 123—124°. *N*-*p*-Tolylbenzaldoxime, when similarly treated, yields at first the above hydrogen tri-iodide, m. p. 137—138°; the action of more hydrogen iodide leads to the formation of a red *hydrogen penta-iodide* (?), m. p. 188—189°. *N*-*p*-Tolylanisaldoxime does not liberate iodine from hydrogen iodide, consequently a periodide is not formed by the action of hydrogen iodide on this *N*-ether; the *hydriodide* is a pale yellow substance, m. p. 77—78°.

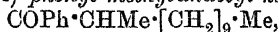
An ethereal solution of *N*-methylbenzaldoxime yields with hydrogen iodide at first the *hydriodide*,  $2C_8H_9ON \cdot HI$ , a yellow, crystalline substance, m. p. 128° (decomp.), and subsequently the *hydriodide*,  $C_8H_9ON \cdot HI$ ,

a pale yellow substance, m. p. 78—79°. The *N*-ether, when treated with iodine in benzene, yields a dark violet *hydrogen penta-iodide*,  $2C_8H_9ON \cdot HI_5$ , m. p. 92°, and a reddish violet *hydrogen tri-iodide*,  $2C_8H_9ON \cdot HI_3$ , m. p. 118°. The former passes into the latter by repeated crystallisation from ethyl iodide.

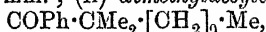
Hydrogen bromide, chloride, and fluoride combine with the *N*-alkylaldoximes in equivalent proportions, yielding salts. Bromine, analogously to iodine, yields perbromides, which have not been thoroughly investigated. W. H. G.

**New Trialkylacetophenones and Trialkylacetic Acids Derived from Them.** ALBIN HALLER and ED. BAUER (*Compt. rend.*, 1909, 149, 5—10. Compare Abstr., 1908, i, 987; this vol., i, 131; Lucas, this vol., i, 488).—The authors have prepared several new trialkylacetophenones by the method already described (this vol., i, 108) with the object of ascertaining the influence of the alkyl groups on the manner in which the ketone undergoes fission when boiled with sodamide. It is found that the decomposition is quite independent of the nature of these groups, and that the products always consist of benzene with the amide of a trialkylacetic acid. *aa*-Dimethyl-*α*-isopropylacetophenone,  $COPh \cdot CMe_2Pr^i$ , b. p. 125—126°/11 mm., forms an *oxime*, crystallising in needles, m. p. 152—153°; on treatment with sodamide it yields *aaβ*-trimethyl-*n*-butyramide,  $CMe_2Pr^i \cdot CO \cdot NH_2$ , pearly leaflets, m. p. 133—134°, forming on hydrolysis with sodium nitrite and sulphuric acid, *aaβ*-trimethyl-*n*-butyric acid,  $C_7H_{14}O_2$ , a

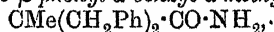
crystalline mass, m. p. 50°, b. p. 104–105°/13 mm. *Phenyl undecyl ketone*,  $\text{COPh} \cdot [\text{CH}_2]_{10} \cdot \text{Me}$ , obtained by the action of lauryl chloride on benzene in presence of aluminium chloride, forms a crystalline mass with an orange-like odour, m. p. 45°, b. p. 201–202°/9 mm.; on methylation it yields (i) *phenyl methylundecyl ketone*,



b. p. 199–200°/9–10 mm.; (ii) *dimethyldecylacetophenone*,



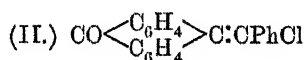
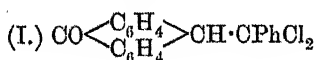
b. p. 198–199°/9 mm. The latter has been converted into *αα-dimethyl-lauric acid*,  $\text{C}_{10}\text{H}_{21} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , m. p. 27°, b. p. 184°/12 mm., the *amide* of which crystallises in pearly scales, m. p. 95–96°. *α-Benzyl-α-dimethylacetophenone*,  $\text{COPh} \cdot \text{CMe}_2 \cdot \text{CH}_2\text{Ph}$ , has b. p. 180–185°/11 mm., and forms an *oxime*, m. p. 191°. *β-Phenyl-αα-dimethylpropionic acid*,  $\text{CH}_2\text{Ph} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , m. p. 57°, b. p. 172–174°/19 mm., forms an *amide*, crystallising in needles, m. p. 62–63°, and a yellow *nitro-derivative*,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$ , m. p. 134°, b. p. 220–230°/20 mm. *α-Dibenzyl-α-methylacetophenone*,  $\text{C}_{23}\text{H}_{23}\text{O}$ , occurs in prisms, m. p. 61°; it has been converted into *β-phenyl-α-benzyl-α-methylpropionamide*,



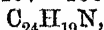
prisms, m. p. 149°; the corresponding acid could not be obtained.

W. O. W.

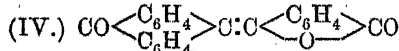
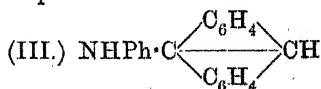
**Reactions of Anthranol.** ROBERT PADOVA (*Compt. rend.*, 1909, 149, 217–220. Compare this vol., i, 167).—When anthranol is heated with tri-*ω*-chlorophenylmethane in toluene, hydrogen chloride is evolved and a small quantity of dianthrone formed together with *dichlorobenzylanthrone* (formula I), small, grey prisms, m. p. 158–159°. Hot pyridine eliminates hydrogen chloride and produces *ω-chlorophenylanthraquinomethane* (formula II), small, rose-coloured prisms, sintering at 128°, m. p. 130–131°; it develops a deep red coloration with sulphuric acid.



When anthranol is heated for thirty minutes with excess of an aromatic amine, condensation occurs, with formation of arylanthramines, compounds crystallising from toluene in yellow needles showing intense fluorescence. *Phenylanthramine* (formula III) sinters at 191°, and has m. p. 197–198°. *α-Naphthylanthramine*,



has m. p. 199–201°; *β-naphthylanthramine* sinters at 205°, and has m. p. 213°.



Anthranol reacts with phthalyl chloride, forming *phthalylideneanthrone* (formula IV), which crystallises in brown spangles, sintering at 259°, m. p. 262–264°, and giving a deep red solution with alcoholic potassium hydroxide.

A 75% yield of dianthrone is obtained by oxidising anthranol with phenanthraquinone (compare Dimroth, *Abstr.*, 1901, i, 198; Meyer, this vol., i, 168).

Diphenylmethylenanthraquinone (*Abstr.*, 1906, i, 741) forms, on reduction with acetic anhydride and zinc dust, 10-acetoxy-9-anthryl-

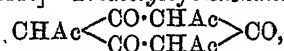
diphenylmethane,  $\text{OAc} \cdot \text{C} \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{C}_6\text{H}_4 \end{array} \text{C} \cdot \text{CHPh}_2$ . This has m. p. 228—229°;

its solutions show an intense violet fluorescence.

Phosphorus pentachloride attacks anthranol, forming a compound, m. p. 298—300°. W. O. W.

**Transformation of a Phloroglucinol Derivative into one of cycloHexantrione.** GUSTAV HELLER (*Ber.*, 1909, 42, 2736—2742).—The author has found that when phloroglucinyl triacetate is heated with zinc chloride to 130°, a molecular change takes place, whereby the triacetate is converted into triacetylcyclohexantrione; this compound yields a tribenzoyl derivative, and with hydroxylamine a monoxime.

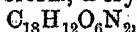
[With OTTO LANGKOPF.]—*Triacetylcyclohexantrione*,



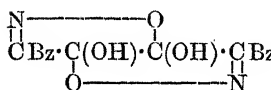
crystallises in colourless, felted needles, m. p. 156°; it gives an intense blood-red coloration with ferric chloride, and a green copper salt; the substance is also produced when a mixture of phloroglucinol, acetic anhydride, and zinc chloride is heated in a closed tube at above 150°.

*Triacetyltribenzoylcyclohexantrione*,  $\text{CAcBz} \begin{array}{c} \swarrow \text{CO} \cdot \text{CAcBz} \\ \searrow \text{CO} \cdot \text{CAcBz} \end{array} \text{CO}$ , has m. p. 220° (decomp.); it gives no coloration with ferric chloride; on hydrolysis with 80% sulphuric acid it yields phloroglucinol. The monoxime of triacetylcyclohexantrione,  $\text{C}_{12}\text{H}_{13}\text{O}_6\text{N}$ , has m. p. 187° (decomp.). Triacetylcyclohexantrione forms two monophenylhydrazones; the  $\alpha$ -compound forms bushy, yellow needles, m. p. 154°, and the  $\beta$ -compound (produced at a higher temperature) forms yellow needles, m. p. 184°. J. C. C.

**Attempts to Convert Oxalyldiacetophenone and other Oxalyl Compounds into Hexaketones.** OSKAR WIDMAN and ERIK VIRGIN (*Ber.*, 1909, 42, 2794—2806).—In the hope of directly oxidising the two methylene groups in oxalyldiacetophenone to carbonyl groups, the substance has been warmed with nitric acid, D 1.4, but the products are Holleman's diphenyldinitrosacyl and isodiphenyldinitrosacyl and an unexamined oil; the first-mentioned compound, which, with the oil, results by the action of nitric acid, D 1.5, at 0°, forms with hydrazine hydrochloride an azine,  $\begin{array}{c} \text{N} : \text{CPh} \cdot \text{C} : \text{N} \cdot \text{O} \\ | \quad | \\ \text{N} : \text{CPh} \cdot \text{C} : \text{N} \cdot \text{O} \end{array}$ , m. p. 207° (decomp.). When nitrous fumes are passed into a suspension of oxalyldiacetophenone in chloroform, a crystalline substance,



m. p. 130° (decomp.), is obtained, which has the composition of



dioximino-oxalyldiacetophenone, but since it is not attacked by nitrous acid or amyl nitrite and does not form a quinoxaline derivative, it receives the annexed constitution, which is in harmony with the de-

composition of the substance into oxalic acid and benzoyl cyanide by cold phenylhydrazine, aniline, hydroxylamine, or pyridine. It is stable to strong mineral acids, and is not attacked by acetyl chloride, acetic anhydride, or phenylcarbimide. 2:4:2':4'-*Tetramethyloxalyldiacetophenone*,  $\text{C}_6\text{H}_5\text{Me}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5\text{Me}_2$ , m. p. 169—170°, obtained from acetyl-*m*-xylene, ethyl oxalate, and sodium ethoxide, and 4:4'-*dimethoxyoxalyldiacetophenone*, m. p. 182°, form dioximino-derivatives, m. p. 113—114° (decomp.) and 122—123° (decomp.) respectively, the properties of which are quite similar to those of the preceding substance.

*Tetrabromo-oxalyldiacetophenone*,  $\text{C}_2\text{O}_2(\text{CBr}_2\cdot\text{COPh})_2$ , m. p. 196—197°, prepared by the action of bromine on a chloroform solution of oxalyldiacetophenone containing anhydrous sodium carbonate, crystallises in stout, yellow prisms, retains the halogen very firmly, and is hydrolysed by sodium hydroxide, yielding methylene bromide and oxalic and benzoic acids.

*Dibromo-oxalyldiacetophenone*,  $\text{C}_2\text{O}_2(\text{CHBr}\cdot\text{COPh})_2$ , m. p. 124—125°, is obtained by passing air and bromine vapour into a chloroform solution of oxalyldiacetophenone containing calcium carbonate.

C. S.

**Action of Sodium Hydroxide on Tetrabromo-*o*-benzoquinone.** C. LORING JACKSON and AUGUSTUS H. FISKE (*Ber.*, 1909, 42, 2636—2638. Compare Zincke, *Abstr.*, 1887, 808).—When tetrabromo-*o*-benzoquinone is treated with cold sodium hydroxide solution (1:5), the products are tetrabromocatechol, m. p. 190—191°, and the *carboxylic acid* derived from the ether of bromotrihydroxycyclopentadiene,  $\text{C}_5\text{HBr}(\text{OH})_3\cdot\text{O}\cdot\text{C}_5\text{Br}(\text{OH})_3\cdot\text{CO}_2\text{H}$ , which separates from glacial acetic acid in pale yellow crystals, m. p. 174° (decomp.). When *N*-sodium hydroxide at 6° is used, the product crystallises from benzene in colourless prisms with acid properties, m. p. 217° (decomp.).

With 0.5*N*-sodium hydroxide at 15° the products are two acids. The one crystallises from benzene, in which it is sparingly soluble, as pale yellow needles, m. p. 207° (decomp.), and the other in colourless, rhombic prisms, m. p. 121° (decomp.). J. J. S.

**Tribromoresoquinone.** RICHARD MEYER and KURT DESAMARI (*Ber.*, 1909, 42, 2814—2824).—The molecular weight of tribromoresoquinone in benzene (compare this vol., ii, 721) points to the bimolecular formula and therefore confirms Zincke and Schwabe's constitution,  $\text{CO} \begin{array}{c} \text{CBr}:\text{CH} \\ \text{CBr}_2\cdot\text{CO} \end{array} \text{C}:\text{C} \begin{array}{c} \text{CH}:\text{CBr} \\ \text{CO}\cdot\text{CBr}_2 \end{array} \text{CO}$ , for this substance. By treatment with tin and hydrochloric acid, hydriodic acid, chloroform, *as*-methyl- or benzoyl-phenylhydrazine, or semicarbazide, it yields 3:5:3':5'-*tetrabromo-2:4:2':4'-diresorcinol*, m. p. 280° (*tetra-acetate*,

m. p. 195°; *tetrabenzoate*, m. p. 188°), identical with the substance obtained by the bromination of Bayer & Co.'s 2:4:2':4'-diresorcinol (*tetra-acetate*, m. p. 120°; *tetrabenzoate*, m. p. 163°), which yields tribromoresorcinone by treatment with bromine in dilute acetic acid. Attempts to debrominate tetrabromodiresorcinol have been unsuccessful, but by prolonged heating of its alcoholic solution with zinc dust a *dibromodiresorcinol*,  $C_{12}H_8O_4Br_2$ , m. p. 195°, has been obtained, which forms a *tetra-acetate*, m. p. 154°, and a *tetrabenzoate*, m. p. 174°.

3:5:3':5'-Diresorcinol (*tetrabenzoate*, m. p. 200°), by bromination in glacial acetic acid, yields *hexabromodiresorcinol*,  $C_{12}H_4O_4Br_6$ , darkening at 180° (*tetra-acetate*, m. p. 259—264°), and by bromination in carbon disulphide forms a *tetrabromodiresorcinol*,  $C_{12}H_6O_4Br_4$ , m. p. 187—195° (*tetra-acetate*, m. p. 170°; *tetrabenzoate*, m. p. 265°). C. S.

**Oxidation of Fenchyl Alcohol.** A. BLUMANN and OTTO ZEITSCHEL (*Ber.*, 1909, 42, 2698—2702).—In the oxidation of fenchyl alcohol to fenchone by sodium dichromate and dilute sulphuric acid; a crystalline substance, m. p. 77—78°, has been obtained in 1—2% yield, which proves to be Czerny's lactone of  $\alpha$ -hydroxydihydrofencholenic acid. The identity is confirmed by converting the lactone into the hydroxy-acid, the hydrochloride, and  $\alpha$ -fencholenic acid. The last appears to be a mixture of isomeric acids differing in the position of the double linking. Attempts to oxidise fenchone to the lactone have been unsuccessful. C. S.

**Philippine Terpenes and Essential Oils. III.** RAYMOND F. BACON (*Philippine J. Sci.*, 1909, 4, 93—132. Compare Abstr., 1908, i, 814, 815; also Clover, *ibid.*, 1907, i, 542).—The source of Manila elemi is *Canarium luzonicum*. When fresh it is soft, but when left on trees exposed to the sun becomes quite hard. The terpenes obtained by distilling more than one hundred different specimens of elemi under reduced pressure have been isolated. The boiling point or specific rotatory powers of the different terpenes vary considerably. Some consist of limonene, others (90%) of phellandrene.

Phellandrene nitrite (Wallach, Abstr., 1904, i, 1035), when crystallised from cold solvents, has m. p. 120—121°.  $\beta$ -Phellandrene also appears to yield the same nitrite. In addition to  $\alpha$ - and  $\beta$ -phellandrenes there appears to be a higher boiling phellandrene in elemi resin. It has b. p. 175—178°,  $D_4^{20}$  0.8375,  $n_D^{20}$  1.4685. The resin obtained after the distillation of the terpenes from elemi has been examined, and also subjected to destructive distillation. As a rule, the neutral product of distillation is an ordinary resin oil, but in two cases the terpene obtained was nearly pure pinene. Others again gave limonene and phellandrene. The halogen derivatives of terpenes react with magnesium, but the Grignard compounds, so formed, do not react normally with ethyl orthoformate.

$\alpha$ -Phellandrene can be transformed into dipentene by boiling its chloride for six hours in a reflux apparatus with excess of alcoholic potassium hydroxide.

Experiments have been made with lemon grass oil; *cinnamomum mercadoi*, which yields safrole, but practically no cinnamaldehyde;

petroleum nuts (fruits of *Pittosporum resiniferum*, which gave heptane and dihydroterpene; vetiver oil, from the roots of *Andropogon squarrosus* (compare Abstr., 1903, i, 187), which yielded an acid  $C_{14}H_{24}O_2$ ; balao resin from *Dipterocarpus vernicifluus* and *D. grandiflorus*, which yields a sesquiterpene, b. p. 118—119°/8 mm.,  $D_4^{20}$  0.9104,  $n_D^{20}$  1.4956,  $[\alpha]_D^{30} + 116.4^\circ$ ; *Lantana camara*; oil of Ylang-ylang.

J. J. S.

**Constitution of isoPinene.** OSSIAN ASCHAN (Reprint from *Öfversigt Finska Vetensk. Soc. Förhandl.*, 1908–1909, 51, A, No. 9).—The terpene described previously as pinolene (Abstr., 1907, i, 630) is shown to be a mixture of two hydrocarbons, since part of it ( $\alpha$ -pinolene) is removed by treatment with aqueous potassium permanganate, whilst the remainder,  $\beta$ -pinolene, remains unattacked.  $\beta$ -Pinolene is a colourless liquid, b. p. 142—144°,  $D_4^{20}$  0.8588,  $[\alpha]_D + 0.28^\circ$ ,  $n_D^{20}$  1.44769, mol. ref. 42.37. The latter value indicates that the mol. of  $\beta$ -pinolene is built up of three carbon ring systems, of which one is a cyclopropane ring. The hydrochloride has m. p. 25—26°, and is apparently different from the hydrochloride obtained from crude pinolene (*loc. cit.*); however, when treated with aniline it yields isopinene. The acid formed by the oxidation of  $\alpha$ -pinolene with potassium permanganate has been identified as *r*-camphoric acid.

isoPinene has b. p. 154.5—155.5°,  $D_4^{20}$  0.8658,  $n_D^{20} + 2.61^\circ$  (in 1-dm. tube),  $n_a$  1.470253, mol. ref. 43.48, and is therefore probably a dicyclic terpene with a double linking. In fact, isopinene

probably has the annexed constitution, since it is converted by aqueous potassium permanganate into apocamphoric acid and fenchonic acid, which has

the formula  $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COMe} \\ | \\ \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \\ | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{COMe} \end{array}$ , for it yields apocamphoric acid when

treated with potassium hydroxide and bromine. Fenchonic acid crystallises in small, thick leaflets and prisms, m. p. 126—128°, and yields a somewhat unstable phenylhydrazone, crystallising in orange-yellow, long, six-sided leaflets, m. p. 70—100°. It is proposed to use von Baeyer's nomenclature, whereby isopinene becomes 2:7:7-trimethyl-2-norcamphene.

W. H. G.

**Chitin.** D. H. WESTER (*Arch. Pharm.*, 1909, 247, 282—307).—The author gives an exhaustive list of the researches on chitin since 1811, and a full account of its distribution in the animal and vegetable kingdoms. The chitin from different sources is shown to be one and the same substance. The method of isolation differs slightly from the following, according to the nature of the source. Shrimp shells are treated with cold 5% acetic acid, to destroy carbonates, and with 5% hydrochloric acid, at first for three hours at the ordinary temperature and finally for fifteen minutes on the water-bath with a fresh portion of the acid, whereby the next operation, the extraction of the colouring matters by hot alcohol, is facilitated. The residue is treated on the water-bath for five hours with frequently renewed 5%, and finally for one hour with 10%, potassium hydroxide, collected, washed, dried, and

extracted with ether. After treatment with dilute acid to remove chitosan, the residue is fairly pure chitin; its complete purification has probably not yet been accomplished. The susceptibility to the attack of alkali hydroxides, whereby chitosan is formed, is probably the reason for the frequent inaccuracies in the literature regarding the properties and reactions of chitin. Chitin free from chitosan does not decolorise an iodine-starch solution, does not respond to Millon's or the biuret test, does not give a violet coloration with iodine and dilute sulphuric acid, and remains unchanged after six hours' treatment with gastric and pancreatic juices. It is only slowly attacked by dilute mineral acids; from its solutions in 37% hydrochloric acid, or 50% nitric acid, it can be more or less recovered by careful neutralisation at 0°, even after many hours, but is decomposed by 95% sulphuric acid in less than thirty minutes. As tests for chitin, the author uses (1) its conversion by potassium hydroxide into chitosan, which (a) gives a violet coloration with 0.5% iodine and 1% sulphuric acid solution, (b) is precipitated as the sulphate from acetic acid solution by 1% sulphuric acid; (2) solubility in, and recovery from, 50% nitric acid; (3) formation of glucosamine hydrochloride by boiling concentrated hydrochloric acid.

A 5% solution of potassium hydroxide in one hour at 160° converts chitin into chitosan, ammonia, acetic and oxalic acids, and smaller amounts of formic, butyric, and tartaric acids. Saturated potassium hydroxide at 250° for one hour yields a non-nitrogenous residue, indole, ammonia, acetic, formic, and oxalic acids, and traces of butyric and tartaric acids. When treated with 40–60% potassium hydroxide, chitin is completely changed into chitosan, within one hour at 110–160° and after 90–100 days at the ordinary temperature.

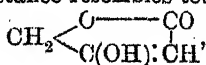
Chitosan,  $C_{14}H_{26}O_{10}N_2$ , is best prepared by treating chitin with 50% potassium hydroxide at 160–170° for one hour, dissolving the mass in 2.5–3% acetic acid, and reprecipitating the chitosan by a slight excess of alkali. It is soluble in many organic acids, and is precipitated from such solutions by 1% sulphuric acid. Its nitrogen is evolved quantitatively by nitrous acid.

C. S.

**Assamin.** JOSEF HALBERKANN (*Biochem. Zeitsch.*, 1909, 19, 310–367).—*Assamin*,  $C_{30}H_{46}O_{15}$  or  $C_{60}H_{92}O_{30}$ , a neutral saponin prepared from Assam tea seeds, is obtained as a yellowish-white, amorphous powder, is optically inactive, and yields an *acetyl* derivative, probably  $C_{30}H_{36}O_{15}Ac_{10}$ , which is also amorphous. On acid hydrolysis it yields a mixture of sapogenins, galactose, arabinose, and probably some butyric acid. A full description of its pharmacological characters is given. It is a strong hæmolytic agent. W. D. H.

**The Benzotetronic Acid [4-Hydroxycoumarin] Group. I.** RICHARD ANSCHÜTZ (*Annalen*, 1909, 367, 169–270).—An account of an exhaustive investigation on the preparation and properties of benzotetronic acid and its derivatives. Benzotetronic acid is 4-hydroxycoumarin,  $C_6H_4$   $\begin{smallmatrix} \diagup O \\ \diagdown C(OH):CH \end{smallmatrix}$   $\begin{smallmatrix} \diagup CO \\ \diagdown \end{smallmatrix}$ , but the use of the former name is

advocated, since this substance resembles tetronic acid,



to a remarkable degree, not only in its structure, but in its reactions. A new synthesis of coumarin is also described.

[With RICHARD ANSPACH, REMIGIUS FRESSENIUS, and REINHOLD CLAUS.]—I. *Condensations with Acetylsalicylyl Chloride*.—3-Carboethoxybenzotetronic acid (ethyl 4-hydroxycoumarin-3-carboxylate),

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \text{:} \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$ , is prepared by the condensation of acetylsalicylyl chloride with ethyl sodiomalonate; it crystallises in white, prismatic needles, m. p.  $101^\circ$ ; the ammonium salt,  $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}$ , forms tufts of white needles; the sodium salt,  $\text{C}_{12}\text{H}_9\text{O}_5\text{Na}$ , is a white powder; the copper salt,  $(\text{C}_{12}\text{H}_9\text{O}_5)_2\text{Cu}$ , is a blue, crystalline powder; the silver salt is a white powder.

Ethyl sodiocyanoacetate and acetylsalicylyl chloride interact, yielding ethyl  $\alpha$ -cyano- $\alpha$ -acetoxybenzoylacetate,  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}$  or  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) \text{:} \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et}$ , which crystallises in small, white leaflets, m. p.  $65^\circ$ . It is converted by ammonium hydroxide into

ammonium 3-cyanobenzotetronate,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{ONH}_4) \text{:} \text{C} \cdot \text{CN} \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$ ; the acid (3-cyano-4-hydroxycoumarin),  $\text{C}_{10}\text{H}_5\text{O}_3\text{N}$ , forms crystalline nodules, m. p.  $242^\circ$ .

3-Carboxylamidobenzotetronic acid (4-hydroxycoumarin-3-carboxylamide),  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{C}(\text{OH}) \text{:} \text{C} \cdot \text{CO} \cdot \text{NH}_2 \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$ , is prepared by the action of concentrated sulphuric acid on the nitrile just described; it crystallises in tufts of needles, m. p.  $219^\circ$ .

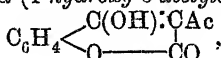
3-Ethylcarboxybenzotetronic acid is converted by phosphorus pentachloride into the corresponding chloride (ethyl 4-chlorocoumarin-3-carboxylate),  $\text{C}_{12}\text{H}_9\text{O}_4\text{Cl}$ , crystallising in almost white, flat needles, m. p.  $83\text{--}5^\circ$ . The latter substance, when treated with an alcoholic solution of sodium ethoxide, yields ethyl 4-ethoxycoumarin-3-carboxylate,  $\text{C}_{14}\text{H}_{14}\text{O}_5$ , a crystalline substance, m. p.  $123\text{--}5\text{--}124\text{--}5^\circ$ , which is hydrolysed by alcoholic potassium hydroxide, yielding 4-ethoxycoumarin-3-carboxylic acid,  $\text{C}_{12}\text{H}_{10}\text{O}_5$ , white needles, m. p.  $86^\circ$ . Attempts to prepare 4-ethoxycoumarin from the latter substance by elimination of carbon dioxide were unsuccessful.

Benzotetron-3-carboxylanilide (4-hydroxycoumarin-3-carboxylanilide),  $\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}$ , is prepared by the action of boiling aniline on ethyl 4-hydroxycoumarin-3-carboxylate; it crystallises in tufts of slender, white needles, m. p.  $213^\circ$ ; the sodium derivative,  $\text{C}_{16}\text{H}_{10}\text{O}_4\text{NNa}$ , formed by the action of sodium on a solution of the substance in benzene, is a white, amorphous substance, which turns brown at  $300^\circ$ ; the silver derivative,  $\text{C}_{16}\text{H}_{10}\text{O}_4\text{NAg}$ , is a white powder; it is not known whether the metal in these compounds is attached to oxygen or nitrogen. 3-Carboethoxybenzotetronanilide (ethyl 4-anilinocoumarin-3-carboxylate),  $\text{C}_{18}\text{H}_{15}\text{O}_4\text{N}$ , is formed by the action of an alcoholic solution of aniline on ethyl 4-chlorocoumarin-3-carboxylate; it forms flat, pale yellow, prismatic needles, m. p.  $128^\circ$ . 4-Anilinocoumarin-3-carboxylanilide,  $\text{C}_{22}\text{H}_{16}\text{O}_3\text{N}_2$ , is formed by boiling the substance just described with an alcoholic solution of aniline; it crystallises in tufts of slender, yellow needles, m. p.  $194^\circ$ . The following compounds are

prepared by using phenylhydrazine instead of aniline: *4-hydroxycoumarin-3-carboxylic acid phenylhydrazide*,  $C_{16}H_{12}O_4N_2$ , feathery, pale yellow crystals, m. p.  $210^\circ$ ; *ethyl 4-phenylhydrazinocoumarin-3-carboxylate*,  $C_{18}H_{16}O_4N_2$ , small, felted needles, m. p. about  $220^\circ$  (decomp.); *4-phenylhydrazinocoumarin-3-carboxylic acid phenylhydrazide*,

$C_{22}H_{18}O_3N_4$ , faintly yellow, slender crystals, m. p.  $189-190^\circ$  (decomp.).

*3-Acetobenzotetronic acid (4-hydroxy-3-acetylcoumarin)*,



is prepared by the action of acetylsalicyl chloride on ethyl sodio-acetoacetate; it forms slender, white needles, m. p.  $134^\circ$ ; the ammonium, sodium, and silver salts were analysed.

*Benzotetronic acid (4-hydroxycoumarin)* may be prepared by heating ethyl 4-hydroxycoumarin-3-carboxylate with aqueous potassium hydroxide; similarly, from ethyl 4-ethoxycoumarin-3-carboxylate, 3-cyano-4-hydroxycoumarin and 4-hydroxy-3-acetylcoumarin; the silver salt,  $C_9H_5O_3Ag$ , is a white powder, which, when heated with ethyl iodide, yields *4-ethoxycoumarin*,  $C_{11}H_{10}O_3$ , crystallising in pale yellow leaflets, m. p.  $136^\circ$ , b. p.  $174^\circ/14$  mm. *4-Acetoxy coumarin*,  $C_{11}H_8O_3$ , prepared by the action of acetic anhydride on benzotetronic acid, crystallises in slender needles, m. p.  $103^\circ$ . *Benzotetronyl chloride (4-chlorocoumarin)*,

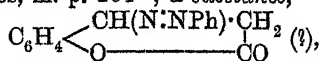
$C_6H_4 \begin{array}{c} \diagup CCl \cdot CH \\ \diagdown O \text{---} CO \end{array}$ , is formed by the action of phosphorus pentachloride on a solution of benzotetronic acid in chloroform; it crystallises in long, white needles, m. p.  $91-92^\circ$ , b. p.  $163-165^\circ/12$  mm., and is not decomposed by water or alcohol; the corresponding bromide,

$C_9H_5O_3Br$ , has m. p.  $90-91^\circ$ , b. p.  $174-177^\circ/14$  mm., and is likewise not decomposed by water. The chloride or bromide, when treated with zinc dust and alcohol, yields coumarin.

The following compounds are prepared by heating benzotetronic acid, its chloride or bromide with the necessary amine: *benzotetron-anilide (4-anilinocoumarin)*,  $C_{15}H_{11}O_2N$ , glistening, yellow leaflets, m. p.  $259-260^\circ$ ; the *o-toluidino*-compound,  $C_{16}H_{13}O_2N$ , pale yellow, prismatic plates, m. p.  $214-216^\circ$ ; the *piperidino*-compound,

$C_{14}H_{15}O_2N$ , white, flat, prismatic needles, m. p.  $104-105^\circ$ .

The action of phenylhydrazine on benzotetronic acid or its bromide leads to the formation of three substances: *benzotetronic acid phenylhydrazide (4-phenylhydrazinocoumarin) (?)*,  $C_{15}H_{12}O_2N_2$ , white, glistening, prismatic needles, m. p.  $201^\circ$ ; a substance,



red needles, m. p.  $186^\circ$ ; a substance,  $C_{15}H_{12}O_2N_2$ , small, yellowish-red crystals, m. p. about  $120^\circ$ .

*3-Oximinocoumarin*,  $C_6H_4 \begin{array}{c} \diagup CO \cdot C \cdot N \cdot OH \\ \diagdown O \text{---} CO \end{array}$ , prepared by the action of nitrous acid on benzotetronic acid, crystallises in glistening, golden-yellow leaflets, m. p.  $149^\circ$  (decomp.); the solutions in aqueous alkalis

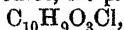
are first blue, but turn yellow in a short time; the *silver* salt,



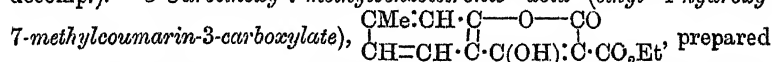
is an emerald-green powder.

Benzotetronic acid, analogously to tetric acid, condenses with formaldehyde, yielding 3-methylenebisbenzotetronic acid (3-methylenebis-4-hydroxycoumarin),  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{C}(\text{OH}) \\ \text{O} \text{---} \text{CO} \quad \text{CO} \text{---} \text{O} \end{array} \text{C}_6\text{H}_4$ , a white, crystalline substance, m. p. about  $260^\circ$  (decomp.), and with acetaldehyde forming the analogous ethylidene compound,  $\text{C}_{20}\text{H}_{14}\text{O}_6$ , m. p.  $165^\circ$ . Condensation products of benzotetronic acid with *n*-propaldehyde, *n*-butyraldehyde, and acetone could not be prepared.

[With JOSEPH WAGNER and PETER JUNKERSDORF.] II. *Condensations with Acetyl-m-cresotyl Chloride* (3-Acetoxy-*p*-toluyl Chloride). — *Acetyl-m-cresotic acid* [2-acetoxy-4-methylbenzoic acid],  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , crystallises in small, white needles, m. p.  $139^\circ$ ; the *chloride*,



forms a white, crystalline mass, m. p.  $15^\circ$ , b. p.  $141^\circ/10$  mm. (slight decomp.). 3-Carbethoxy-7-methylbenzotetronic acid (ethyl 4-hydroxy-7-methylcoumarin-3-carboxylate),

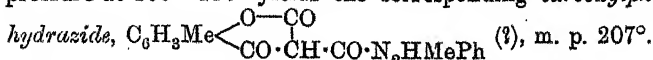


prepared by the interaction of the chloride just described with ethyl sodio-malonate, forms glistening, white leaflets, m. p.  $140^\circ$ ; the *sodium* salt,  $\text{C}_{13}\text{H}_{11}\text{O}_5\text{Na}$ ; *ammonium* salt, small, white needles, m. p.  $230\text{---}240^\circ$  (decomp.); *silver* salt, glistening white needles; and *acetate*,  $\text{C}_{15}\text{H}_{14}\text{O}_6$ , white crystals, m. p.  $217^\circ$ , were prepared.

The following compounds are obtained by treating the silver salt with the necessary alkyl iodide: ethyl 4-methoxy-7-methylcoumarin-3-carboxylate,  $\text{C}_{14}\text{H}_{14}\text{O}_5$ , forms small, white needles, m. p.  $126^\circ$ ; the analogous 4-ethoxy-derivative,  $\text{C}_{15}\text{H}_{16}\text{O}_5$ , forms pale yellow, transparent, monoclinic crystals, m. p.  $104^\circ$ ; the 4-propoxy-compound,  $\text{C}_{16}\text{H}_{18}\text{O}_5$ , forms pale yellow, transparent, monoclinic crystals, m. p.  $112^\circ$ . Attempts to prepare the isomeride of the ethoxy-compound having the

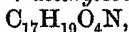
constitution  $\text{C}_6\text{H}_5\text{Me} \begin{array}{c} \text{O} \text{---} \text{CO} \\ \text{CO} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \end{array}$  by condensing ethyl sodio-ethylmalonate with acetyl-*m*-cresotyl chloride were unsuccessful.

Ethyl 4-hydroxy-7-methylcoumarin-3-carboxylate is converted (1) by aniline at  $175^\circ$  into 7-methylbenzotetron-3-carboxylanilide (4-hydroxy-7-methylcoumarin-3-carboxylanilide),  $\text{C}_{17}\text{H}_{13}\text{O}_4\text{N}$ , a yellow substance, m. p.  $202^\circ$ ; (2) by phenetidine at  $200^\circ$  into the analogous phenetidide,  $\text{C}_{19}\text{H}_{17}\text{O}_5\text{N}$ , slender, very pale yellow needles, m. p.  $218^\circ$ ; (3) by an alcoholic 33% solution of ethylamine into the corresponding ethyl-carboxylanilide,  $\text{C}_{13}\text{H}_{13}\text{O}_4\text{N}$ , small, silvery crystals, m. p.  $152^\circ$ ; (4) by an alcoholic solution of phenylhydrazine into the carboxylphenylhydrazide,  $\text{C}_{17}\text{H}_{14}\text{O}_4\text{N}_2$ , small crystals, m. p.  $232^\circ$ ; the latter substance when heated with a solution of methyl iodide in methyl alcohol under pressure at  $100\text{---}110^\circ$  yields the corresponding carboxylphenylmethy-



The ester is converted by phosphorus pentachloride into ethyl 4-chloro-7-methylcoumarin-3-carboxylate,  $\text{C}_{13}\text{H}_{11}\text{O}_4\text{Cl}$ , a yellow substance,

m. p. 109—110°, which, when treated with an alcoholic solution of aniline, yields *ethyl 4-anilino-7-methylcoumarin-3-carboxylate*,

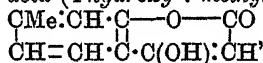


m. p. 162°, and when heated with aniline at 184° yields *4-anilino-7-methylcoumarin-3-carboxylanilide*,  $\text{C}_{23}\text{H}_{18}\text{O}_3\text{N}$ , m. p. 220—222°.

*3-Acetyl-7-methylbenzotetronic acid* (*4-hydroxy-3-acetyl-7-methylcoumarin*),  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{O} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \cdot \text{CAc} \end{array}$ , prepared by the action of an ethereal solution of acetyl-*m*-cresotyl chloride on ethyl sodioacetoacetate, crystallises in yellow needles, m. p. 136°; the *sodium*, *ammonium* (m. p. 198°), and *silver* salts were analysed; the *methyl* ether,  $\text{C}_{13}\text{H}_{13}\text{O}_4$ , forms pale yellow needles, m. p. 138°; the *ethyl* ether,  $\text{C}_{14}\text{H}_{14}\text{O}_4$ , crystallises in brownish-yellow needles, m. p. 133°; the *propyl* ether,  $\text{C}_{15}\text{H}_{16}\text{O}_4$ , forms dark yellow needles, m. p. 135°.

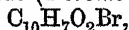
*3-Cyano-7-methylbenzotetronic acid* (*3-cyano-4-hydroxy-7-methylcoumarin*),  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CN} \\ \diagup \quad \diagdown \\ \text{O} \text{---} \text{CO} \end{array}$ , is prepared by the interaction of ethyl sodiocyanoacetate and acetyl-*m*-cresotyl chloride in ethereal solution; it is an amorphous powder, m. p. 250°; the *sodium* and *silver* salts were analysed; the *methyl* ether,  $\text{C}_{12}\text{H}_9\text{O}_3\text{N}$ , crystallises in small, yellow needles, m. p. 238°; the *ethyl* ether,  $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}$ , forms yellow needles, m. p. 218°; the *propyl* ether,  $\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}$ , is a greyish-yellow substance, m. p. 223°.

*7-Methylbenzotetronic acid* (*4-hydroxy-7-methylcoumarin*),



is prepared by heating ethyl 4-hydroxy-7-methylcoumarin-3-carboxylate with a 10% aqueous solution of potassium hydroxide; it forms small, white needles, m. p. 217°; the *silver* salt is a white powder; the *methyl* ether,  $\text{C}_{11}\text{H}_{10}\text{O}_3$ , forms small needles, m. p. 162°; the *ethyl* ether,  $\text{C}_{12}\text{H}_{12}\text{O}_3$ , forms tufts of pale yellow needles, m. p. 144°; the *propyl* ether,  $\text{C}_{13}\text{H}_{14}\text{O}_3$ , has m. p. 148°; the *acetate*,  $\text{C}_{12}\text{H}_{10}\text{O}_4$ , crystallises in slender, white needles, m. p. 142°.

*7-Methylbenzotetronyl bromide* (*4-bromo-7-methylcoumarin*),



forms yellowish-white needles, m. p. 149—150°, b. p. 185—195°/12 mm., and when treated with zinc dust and alcohol yields *7-methyl-*

*coumarin* (*m-cresocoumarin*),  $\text{CMe} \cdot \text{CH} \cdot \text{C} \text{---} \text{O} \text{---} \text{CO}$   
 $\text{CH} = \text{CH} \cdot \text{C} \cdot \text{CH} \cdot \text{CH}$ , a white substance,

m. p. 119—120°. From the bromide are obtained: *4-ethylamino-7-methylcoumarin*,  $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$ , slightly yellow leaflets, m. p. 174°; *4-anilino-7-methylcoumarin*,  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$ , small crystals with a green shimmer, m. p. 247° (decomp.); *4-(p)-toluidino-7-methylcoumarin*,  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ , has m. p. 252°.

The following compounds are prepared by condensing the acid with the necessary aldehyde: *methylenebis-4-hydroxy-7-methylcoumarin*,

$\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{O} \text{---} \text{CO} \quad \text{CO} \text{---} \text{O} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CH}_2 \cdot \text{C} \cdot \text{C}(\text{OH}) \end{array} \text{C}_6\text{H}_3\text{Me}$ , long, white needles,

m. p. 273—275°; *ethylidenebis-4-hydroxy-7-methylcoumarin*,  $\text{C}_{22}\text{H}_{18}\text{O}_6$ , m. p. 206°; *benzylidenebis-4-hydroxy-7-methylcoumarin*,  $\text{C}_{27}\text{H}_{20}\text{O}_6$ ,

m. p. 230°. The acid does not yield a condensation product with propaldehyde.

[With JULIUS SIEBEN.]—III. *Condensations with Acetyl-p-cresotyl Chloride* (4-Acetoxy-m-tolyl Chloride).—The compounds described later are obtained by methods similar to those already described.

*Acetyl-p-cresotic acid* (2-acetoxy-5-methylbenzoic acid),  $C_{10}H_{10}O_4$ , forms small, glistening needles, m. p. 142—143°; the *chloride* has m. p. 47°, b. p. 147°/12 mm. *Ethyl 4-hydroxy-6-methylcoumarin-3-carboxylate*,  $C_{13}H_{12}O_5$ , forms small, thin needles, m. p. 121—122°; the *sodium*, *ammonium*, and *silver* salts were prepared and analysed; the *ethyl ether*,  $C_{15}H_{16}O_5$ , forms small needles, m. p. 87°. *3-Cyano-4-hydroxy-6-methylbenzotetronic acid* (3-cyano-4-hydroxy-6-methylcoumarin),  $C_{11}H_8O_3N$ , has m. p. 248° (decomp.); the *sodium* and *silver* salts were analysed. *3-Acetyl-4-hydroxy-6-methylcoumarin*,  $C_{13}H_{10}O_4$ , forms pale yellow plates, m. p. 144—145°; the *sodium* and *silver* salts were analysed.

*6-Methylbenzotetronic acid* (4-hydroxy-6-methylcoumarin),  $C_{10}H_8O_3$ , crystallises in small, white needles, m. p. 241° (decomp.); the *ethyl ether*,  $C_{12}H_{12}O_3$ , forms small, white needles, m. p. 195°.

[With JOACHIM GRAFF.]—IV. *Condensations with 3-Acetoxy-2-naphthoic Acid*.—3-Acetoxy-2-naphthoic chloride,  $OAc \cdot C_{10}H_6 \cdot COCl$ , forms white crystals, m. p. 89°; the *amide*,  $OAc \cdot C_{10}H_6 \cdot CO \cdot NH_2$ , is a yellowish-green, crystalline substance, m. p. 192°; the *anilide*,  $C_{19}H_{15}O_3N$ , crystallises in small, white needles, m. p. 152°. *3-Carboethoxy-(2:3)-naphthatetronic acid* [ethyl 4-hydroxy- $\beta\beta$ -naphthapyrone-3-carboxylate],  $C_{10}H_6 \begin{smallmatrix} C(OH):C \cdot CO_2Et \\ \diagdown \quad \diagup \\ O \quad CO \end{smallmatrix}$ , forms pale yellow, matted

needles and slender leaflets, m. p. 182°; when treated with aqueous potassium hydroxide it yields 3-hydroxy-2-naphthoic acid and a yellow substance,  $C_{12}H_{12}O_2$  or  $C_{13}H_{10}O_2$ , m. p. 115°. The *ammonium*, *sodium*, *silver*, and *copper* salts were analysed; the *methyl ether*,  $C_{17}H_{14}O_5$ , forms pale yellow crystals, m. p. 146°; the *acetate*,  $C_{18}H_{14}O_6$ , has m. p. 157°. The ester is converted by phenylhydrazine into the *phenylhydrazide*,

$C_{10}H_6 \begin{smallmatrix} CO \cdot CH \cdot CO \cdot NH \cdot NHPh \\ \diagdown \quad \diagup \\ O \quad CO \end{smallmatrix}$ , small, reddish-yellow, felted needles,

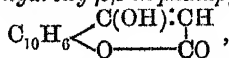
m. p. 245°. *Ethyl 3-acetoxy-2-naphthoylecyanouacetate*,

$OAc \cdot C_{10}H_6 \cdot CO \cdot CH(CN) \cdot CO_2Et$ , crystallises in red leaflets, m. p. 103°. *3-Cyano-(2:3)-naphthatetronic acid* [3-cyano-4-hydroxy- $\beta\beta$ -naphthapyrone],  $C_{10}H_6 \begin{smallmatrix} C(OH):C \cdot CN \\ \diagdown \quad \diagup \\ O \quad CO \end{smallmatrix}$ , is a

yellow powder, m. p. 276°; the *sodium* and *copper* salts were analysed; the *acetate*,  $C_{10}H_9O_4N$ , forms brown crystals, m. p. 229°.

*4-Hydroxy- $\beta\beta$ -naphthapyrone-3-carboxylamide*,  $C_{14}H_9O_4N$ , forms yellow crystals, m. p. 256°. *4-Hydroxy-3-acetyl- $\beta\beta$ -naphthapyrone*,

$C_{10}H_6 \begin{smallmatrix} C(OH):CAc \\ \diagdown \quad \diagup \\ O \quad CO \end{smallmatrix}$ , crystallises in golden-yellow spangles, m. p. 239°; the *sodium*, *copper*, and *silver* salts were analysed. (2:3)-*Naphthatetronic acid* [4-hydroxy- $\beta\beta$ -naphthapyrone],



crystallises in small, white needles, m. p. 240°. 3:3-Methylenebis-4-

hydroxy- $\beta\beta$ -naphthapyrone,  $C_{27}H_{16}O_6$ , is a white substance, m. p. above  $280^\circ$ .

[With AUGUST NEFGEN.]—V. Action of 5-Chloro-2-acetoxybenzoyl Chloride on Ethyl Sodiomalonate.—5-Chloro-2-acetoxybenzoic acid,  $OAc \cdot C_6H_3Cl \cdot CO_2H$ , has m. p.  $148^\circ$ . The chloride,  $C_6H_3O_3Cl_2$ , is a crystalline substance, m. p.  $45^\circ$ , and when treated with ethyl sodiomalonate yields 3-ethylcarboxy-6-chlorobenzotetronic acid (ethyl 6-chloro-4-hydroxycoumarin-3-carboxylate),  $C_{12}H_9O_5Cl$ , crystallising in silky, white needles, m. p.  $175^\circ$ .  
W. H. G.

Pyryl Salts formed with Oxygen Acids. II. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 787—790. Compare this vol., i, 599).—When a dilute acetic acid solution of dinaphthapyranol is treated with excess of a dilute acetic acid solution of picric acid, *dinaphthapyranol picrate*,  $C_6H_2(NO_2)_3 \cdot O \cdot CH \langle \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} \rangle O$ , separates in brilliant, reddish-violet crystals, m. p. above  $220^\circ$  (decomp.), which detonate with difficulty when struck. The substance is a true salt analogous to potassium picrate, but not with the additive compounds which picric acid forms with hydrocarbons, etc. Dinaphthapyranol picrate oxidises boiling ethyl alcohol with the production of acetaldehyde and dinaphthaxanthone, thus:  $C_3H_6O + C_6H_2(NO_2)_3 \cdot O \cdot CH \langle \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} \rangle O = C_2H_4O + CH_2 \langle \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} \rangle O + C_6H_2(NO_2)_3 \cdot OH$ .

[With P. BERTRAND.]—*Dinaphthapyryl sulphate*,  $OH \cdot SO_2 \cdot O \cdot CH \langle \begin{smallmatrix} C_{10}H_6 \\ C_{10}H_6 \end{smallmatrix} \rangle O \cdot H_2SO_4$ , obtained by dissolving the pyranol in hot dilute sulphuric acid and cooling, crystallises with a molecule of sulphuric acid in red crystals, which form several hydrates. The sulphate, like the picrate, oxidises alcohol to acetaldehyde; it reacts with potassium iodide solution, forming bisdinaphthapyryl,  $C_{42}H_{26}O_2$ , and *dinaphthapyryl tri-iodide*,  $C_{27}H_{13}OI_3$ , red crystals, having a green reflex. The oxidising properties of these salts tend to support Haller and Fosse's annexed formula, analogous to the peroxide formula,  $HO \cdot O \cdot SO_2 \cdot OH$ , of Caro's acid. The capacity of dinaphthapyryl sulphate to crystallise with sulphuric acid and with water is analogous to that of the alkali hydrogen sulphates.

*Dinaphthapyryl chromate* is a bright red precipitate, which separates when acetic acid solutions of the pyranol and chromic anhydride are mixed. *Dinaphthapyryl nitroprusside*, obtained by mixing acetic acid solutions of the pyryl bromide and sodium nitroprusside, forms beautiful cantharidin-green crystals. When dinaphthapyryl bromide is treated with potassium ferricyanide solution, a bright red precipitate containing iron and nitrogen is formed.  
E. H.

Metallic Character of the Dinaphthapyryl Salts. III. Displacement of Hydrogen Chloride from the Pyryl Chloride by Hydrogen Bromide, and Conversely, of Hydrogen Bromide from the Pyryl Bromide by Hydrogen Chloride. IV. Displacement of the Acids from Pyryl Salts by Picric Acid.

V. Precipitation of the Dinaphthapyryl Salts as Sulphide by Hydrogen Sulphide. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 790—797).—When dinaphthapyryl bromide is dissolved in hot hydrochloric acid and the solution cooled, red crystals separate, which, after recrystallisation from acetic acid, consist of pure dinaphthapyryl chloride with a molecule of acetic acid of crystallisation and quite free from bromine. Conversely, by dissolving dinaphthapyryl chloride in hot hydrobromic acid and cooling the solution, it is converted into the bromide, which, after recrystallisation from acetic acid, is free from chlorine. Addition of ferric bromide to the acetic acid solution of the pyryl bromide so prepared gives a crystalline precipitate of the double bromide of iron and dinaphthapyryl.

Addition of a slight excess of picric acid dissolved in 80% acetic acid to a solution of dinaphthapyryl bromide dissolved in the same solvent gives a precipitate of brilliant red crystals of dinaphthapyryl picrate (compare preceding abstract). This reaction is explained by the author by the partial hydrolysis (in aqueous acetic acid solution) of the bromide into hydrogen bromide and dinaphthapyranol, and consequent progressive transformation of the latter into picrate on addition of picric acid. By heating the pure picrate with hydrochloric acid until dissolved, it is converted into the chloride, which separates on cooling, and, after recrystallisation from hydrochloric acid, is free from picric acid.

When a current of hydrogen sulphide is passed through a solution of a dinaphthapyryl salt in a mineral or organic acid, the liquid is rapidly decolorised, and a greyish-rose precipitate of *dinaphthapyryl sulphide*,  $S[\cdot CH:(C_{10}H_6)_2 \cdot O]_2$ , is formed. The latter is deposited from benzene solution in brilliant white crystals, which redden superficially in the air and decompose at 275—280°, the temperature varying with the rate of heating. The action of hydrogen sulphide probably first produces the hydrosulphide, which is afterwards transformed into the neutral sulphide. Dinaphthapyryl sulphide when boiled with hydrochloric acid is converted into the chloride.

E. H.

Electropositive Character of the Dinaphthapyryl Radicle. VI. Extremely Pronounced Aptitude of forming Insoluble or Sparingly Soluble Compounds. VII. Displacement of Potassium, Ammonium, and Alkylammonium Chlorides from their Platinichlorides by the Pyryl Chloride. VIII. Displacement of Potassium from Potassium Picrate by the Oxygenated Base Dinaphthapyranol. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 797—800).—It has been shown previously (*Abstr.*, 1901, i, 604) that chloro- and bromo-dinaphthaxanthone combine with the halide acids, platinic chloride, and mercuric chloride and bromide.

[With LESAGE].—Dinaphthapyryl chloride and bromide are now found to form coloured and generally crystalline compounds with the halide salts of almost all the metals, except those of the alkalis and alkali earths. Halide double salts with platinum, palladium, gold, mercury, copper, lead, uranium, chromium, manganese, iron, cobalt, cadmium, zinc, tin, bismuth, antimony, and arsenic have been prepared. Moreover, in extension of a previous observation (*ibid.*, 1902,

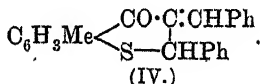
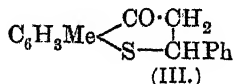
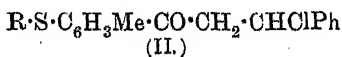
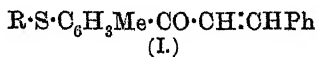
[iii], 27, 496) that several of the reagents for alkaloids precipitate the pyryl halides, it is now found that picric acid, tannin, chlorine, bromine, iodine, chromic anhydride, ammonium perchlorate, potassium iodide, potassium ferrocyanide, potassium ferricyanide, potassium nitroprusside, ammonium thiocyanate, ammonium molybdate, sodium phosphotungstate, and ammonium vanadate give coloured insoluble or sparingly soluble precipitates with the solutions of pyryl salts in dilute halide acids.

When a hydrochloric acid solution of potassium, ammonium, methylammonium, or trimethylammonium platinichloride is treated with a solution of dinaphthapyryl chloride in dilute hydrochloric acid, dinaphthapyryl platinichloride is deposited in red crystals having a golden reflex. These reactions are considered by the author to prove that potassium, ammonium, and alkyl ammonium platinichlorides are partly dissociated in hydrochloric acid solution.

When potassium picrate is treated with an acetic acid solution of dinaphthapyranol, potassium acetate and dinaphthapyryl picrate are formed, probably owing to the partial hydrolysis of the potassium picrate by the acetic acid, and the consequent progressive combination of the pyranol with the liberated picric acid. Conversely, dinaphthapyryl picrate is reconverted by potassium hydroxide solution into potassium picrate and dinaphthapyranol, the equilibrium between the picric acid and the pyranol thus depending on the acidity or alkalinity of the medium.

E. H.

**Transformation of Thiophenol Ethers into Thioflavanone Derivatives.** KARL AUWERS and F. ARNDT (*Ber.*, 1909, 42, 2706—2712).—In extension of their recent work (this vol., i, 175), the authors find that thiophenol ethers can be condensed with benzaldehyde with the formation of thioflavanone derivatives. The condensation is effected by means of dry hydrogen chloride, and, in the case of 6-methyl(or ethyl)-thiol-3-methylacetophenone, proceeds as follows: The benzylidene derivative (I) is first formed and combines with hydrogen chloride to give the compound (II), from which alkyl chloride is eliminated, and the resulting methylthioflavanone (III) condenses with a second molecule of benzaldehyde to yield benzylidene-methylthioflavanone (IV):



The analogous compounds containing oxygen cannot similarly be transformed into flavanone derivatives.

3-Benzylidene-6-methylthioflavanone forms short, stout, bright yellow, glistening prisms and pyramids, m. p. 109—110°, and gives an intense brown coloration with sulphuric acid. The bromide,  $\text{C}_{23}\text{H}_{18}\text{OBr}_2\text{S}$ , crystallises in pale yellow, glistening needles, m. p. 125°; and the hydroxylamine additive product,  $\text{C}_{23}\text{H}_{21}\text{O}_2\text{NS}$  (no oxime is formed),

forms snow-white, glistening needles and plates, m. p. 174—176° (decomp.).

6-Methoxy-3-benzylideneflavanone,  $\text{OMe} \cdot \text{C}_6\text{H}_3 < \begin{matrix} \text{CO} \cdot \text{C} \cdot \text{CHPh} \\ \text{O} - \text{CHPh} \end{matrix}$ , prepared by condensing 6-methoxyflavanone (Abstr., 1904, i, 440) with benzaldehyde in the presence of hydrogen chloride, forms small, stout, glistening crystals, m. p. 118—119°; the hydrochloride crystallises in slender, felted needles, and has m. p. 189°, softening before this point. 3-Benzylidene-6-methylflavanone, similarly prepared from 6-methylflavanone, has m. p. 132—133°. 6-Ethylthiol-3-methylacetophenone,  $\text{C}_{11}\text{H}_{14}\text{OS}$ , prepared from *p*-ethylthioltoluene by the Friedel and Crafts' reaction, crystallises in long, glistening, white needles, m. p. 75·5°. *p*-isoPropylthioltoluene,  $\text{C}_{10}\text{H}_{14}\text{S}$ , prepared from *p*-methylthioltoluene, isopropyl bromide, and sodium, is a colourless oil having a terpene-like odour, b. p. 110°/14 mm., 228°/760 mm. J. C. C.

**Aconitine.** ERNST SCHMIDT [with ARTHUR SCHWANTKE and K. SCHWANTKE] (*Arch. Pharm.*, 1909, 247, 233—243).—Some derivatives of aconitine, m. p. 195—196°, obtained from the tubers of *Aconitum Napellus*, have been examined crystallographically. Aconitine, rhombic [ $a:b:c = 0.54492:1:0.38917$ ]. Aconitine hydrochloride, rhombic [ $a:b:c = 0.87488:1:1.3040$ ]. Aconitine hydrobromide, rhombic [ $a:b:c = 0.86455:1:1.3095$ ]. Ethylpicroaconitine, rhombic [ $a:b:c = 0.97952:1:1.2700$ ]. Aconine hydrochloride, monoclinic, hemimorphous [ $a:b:c = 0.63461:1:1.0374$ ;  $\beta = 90^\circ$ ].

Pseudoaconitine, m. p. 201—202°, from *Aconitum ferox*, must be purified by the repeated crystallisation of its nitrate in order that the regenerated base may separate from dilute methyl alcohol in well-formed, colourless needles.

Japaconitine, from the tubers of *Aconitum Fischeri*, is identical with commercial japaconitine, and different from the alkaloid obtained from *Aconitum Napellus*; it separates from 90% alcohol in crystals identical with those measured by Pope (*Trans.*, 1900, 76, 49). It is remarkable that the hydrochlorides and hydrobromides of japaconitine and aconitine are almost identical, although the two alkaloids are widely different crystallographically (following abstract). C. S.

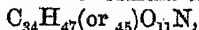
**The Aconitines from Japanese Aconite Tubers.** KOJIRO MAKOSHI (*Arch. Pharm.*, 1909, 247, 243—282).—Since 1877 japaconitine, the alkaloid prepared from Kusauzu tuber-roots obtained in Japan from varieties of the *Aconitum* family, has been examined by several investigators without concordant results. The author gives a full account of the aconitum tubers, of Japanese and Chinese origin, used commercially, and is of opinion that these discordant results are not to be attributed to the different sources from which the japaconitine has been obtained, but, in view of the ready decomposition of the aconite alkaloids, may be due to differences in the methods of isolation and purification of the alkaloid. This view is supported by the m. p.'s of aconitine and japaconitine given by different observers, which, varying between 183° and 204·5°, lead to the conclusion that chemically individual substances have hitherto not been employed.

Two varieties of Kusauzu tubers are recognised: Bushi tubers, obtained from the *Aconitum Fischeri*, grown in Hokkaido (Jeso), and the Kusauzu tubers obtained from a variety of this shrub grown in Hondo. The author commences his attempt to elucidate the mystery of the nature of aconitine (which is asserted by some chemists, and denied by others, to be identical with japaconitine) by a thorough examination of the alkaloid, called jesaconitine, obtained from the Bushi tubers, and japaconitine, prepared from the Kusauzu tubers of Hondo.

A detailed account of the isolation of jesaconitine from Bushi tubers (yield 0.54%) is given. Briefly, the main portion of the alkaloid is obtained by evaporating under 50 mm. pressure to a thin syrup the solution obtained by thrice extracting the coarsely-powdered roots with 96% alcohol for ten days at the ordinary temperature; the syrup is mixed with water, and the bulk of the crude alkaloid precipitated by concentrated sodium carbonate solution. Attempts to obtain the base or its salts in a crystalline form have failed. Jesaconitine must be regarded as benzoylanisoylaconine, since its hydrolysis by water under 8—9 atmospheres yields benzoic and anisic, but not acetic, acids and aconine, the identity of the last, isolated as the hydrochloride, m. p. 175—176°, with the aconine hydrochloride obtained from aconitine being proved by the mixed m. p., by crystallographic examination, and by the formation of tetra-acetylaconine. In four weeks at the ordinary temperature acetyl chloride and jesaconitine yield an *acetyl* derivative,  $C_{40}H_{48}O_{12}NAc_3 \cdot 2H_2O$  (?), m. p. 213—213.5°, which separates from ether in slender needles.

Although more poisonous, jesaconitine is closely related to aconitine (Merck's *aconitine pur. amorph.*) in toxic properties. Its physiological action on dogs and frogs causes the typical paralysis produced by aconitine, but a difference is noticeable in that jesaconitine does not cause mydriasis and salivation in dogs; the local action of the hydrochlorides of the two alkaloids is practically identical.

The extraction of japaconitine from Hondo Kusauzu tubers is very similar to that of jesaconitine from the Bushi tubers. The alkaloid precipitated by sodium carbonate is recrystallised from ether, and finally purified either by repeated crystallisation from methyl alcohol or by the crystallisation of the hydrochloride or hydrobromide. The alkaloid crystallises in needles or small plates, and has m. p. 202.5—203.5°, the same as that of commercial japaconitine purified by the preceding process. The mean value of nine analyses of japaconitine corresponds with the formula of aconitine,



but the two alkaloids are undoubtedly different. The hemihedral crystals of japaconitine hydrochloride, or hydrobromide, have the same angles as the holohedral crystals of the corresponding salts of aconitine. The author confirms in the main the observations of Dunstan and Read (Trans., 1900, 77, 45) on the triacetyl derivative (m. p. 189°, not 166°) and the salts of japaconitine, on pyrojapaconitine, japbenzaconine, and japaconine. The different natures of japaconine and aconine are evident; the former does not form crystallisable salts, and yields a *tetra-acetyl* derivative,  $C_{25}H_{37}(\text{or } 35)O_9N \cdot 4C_2H_3O$ ,

m. p. 236—237°, the *aurichloride* of which, m. p. 253°, crystallises in yellow plates; aconine forms easily crystallisable salts and a tetra-acetyl derivative, m. p. 231—232°, the aurichloride of which is uncrystallisable.

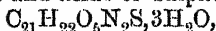
The chief result of the paper is the proof that japaconitine is different from aconitine and from jesaconitine. C. S.

**A New Base Isolated from Ergot of Rye, Ergothionine.** CHARLES TANRET (*Compt. rend.*, 1909, 149, 222—224 \*).—A description of the preparation and properties of a new sulphur-containing base occurring to the extent of 0.1% in ergot of rye. *Ergothionine*,  $C_9H_{15}O_2N_3S \cdot 2H_2O$ , crystallises in colourless, clinorhombic lamellae, m. p. 290° (decomp.), on the Maquenne block;  $[\alpha]_D + 110^\circ$ . It is soluble in 8.6 parts of water at 20°, and insoluble in absolute alcohol or ether. Ergothionine is a feeble base, and forms well defined salts, which in aqueous solution give precipitates with mercuric chloride, potassium mercuric iodide, and platinic chloride in excess, but not with picric or tannic acids.

The *hydrochloride*,  $C_9H_{15}O_2N_3S \cdot HCl \cdot 2H_2O$ , occurs in orthorhombic crystals,  $[\alpha]_D + 88.5^\circ$ ; the anhydrous salt has m. p. 250°; its solution gives with silver nitrate a curdy precipitate having the composition  $[(C_9H_{15}O_2N_3S)_2Ag_2O](AgCl)_2$ . The *sulphate*,  $(C_9H_{15}O_2N_3S)_2 \cdot H_2SO_4 \cdot 2H_2O$ , has  $[\alpha]_D + 87.4^\circ$ . The *phosphate*,  $C_9H_{15}O_2N_3S \cdot H_3PO_4$ , has  $[\alpha]_D + 83.8^\circ$ . The *mercurichloride*,  $C_9H_{15}O_2N_3S \cdot HgCl_2 \cdot HCl$ , is crystalline.

W. O. W.

**Strychnine Alkaloids. V. Isomeric Strychninesulphonic Acids.** HERMANN LEUCHS and WILHELM SCHNEIDER (*Ber.*, 1909, 42, 2681—2685. Compare Abstr., 1908, i, 563; this vol., i, 120, 253, 602).—An aqueous solution of strychnine, containing sulphur dioxide, is treated at 40—50° with precipitated manganese dioxide until the latter has dissolved. By cooling to 20°, acicular crystals of the strychninesulphonic acid already described (this vol., ii, 120) are obtained. By keeping the mother liquor overnight at 0°, a second *strychninesulphonic acid*,  $C_{21}H_{22}O_5N_2S \cdot 2H_2O$ , is obtained in stout prisms, which darkens at 300°, has m. p. 370° (decomp.), and has  $[\alpha]_D^{20} - 138^\circ$  in aqueous solution. From the concentrated filtrate, after removal of the manganese and acids of sulphur, a third *acid*,



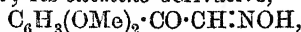
is obtained, which crystallises from boiling water in brilliant, flattened polyhedra or quadratic plates, has m. p. 276° (decomp. corr.), and  $[\alpha]_D^{20} 163.3^\circ$  in aqueous solution.

In the authors' opinion four isomeric strychninesulphonic acids should exist, of which two are stereoisomerides. C. S.

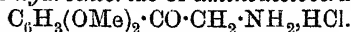
**Synthesis of Papaverine.** AMÉ PICTET and A. GAMS (*Compt. rend.*, 1909, 149, 210—212. Compare this vol., i, 323).—Attempts to prepare papaverine by dehydration of a compound containing 2H less than homoveratroylhomoveratrylamine were unsuccessful, owing to the instability of the parent *base*,  $C_6H_3(OMe)_2 \cdot CH:CH \cdot NH_2$ . The synthesis has been accomplished, however, as follows: veratrole is

\* and *J. Pharm. Chim.*, 1909, [vi], 30, 145—153.

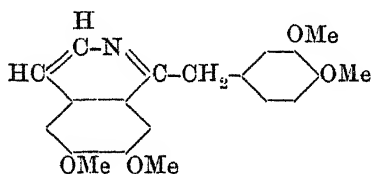
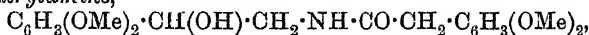
treated with acetyl chloride and aluminium chloride, whereby aceto-veratrone is produced; its *oximino*-derivative,



has m. p.  $131^\circ$ . On reduction with stannous chloride and hydrochloric acid, this yields the *hydrochloride of aminoacetoveratrone*,



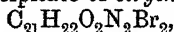
The free base is unstable. The hydrochloride is shaken with homoveratroyl chloride and aqueous sodium hydroxide, when *homoveratroyl-aminoacetylveratrone*,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe})_2$ , is obtained in brilliant spangles, m. p.  $142^\circ$ . On reduction with sodium amalgam in alcoholic solution, it furnishes *homoveratroylhydroxy-homoveratrylamine*,



colourless needles, m. p.  $124^\circ$ . When this is boiled in xylene with anhydrous phosphoric acid,  $2\text{H}_2\text{O}$  is eliminated and a substance formed which is identical with natural papaverine. This synthesis completely establishes the annexed constitution for the alkaloid.

W. O. W.

**Bromination of Strychnine, Brucine, and other Alkaloids.** JÓZEF BURACZEWSKI and M. DZIURZYŃSKI (*Bull. Acad. sci. Cracow*, 1909, 632—641).—When bromine dissolved in carbon disulphide is added slowly to a cold saturated alcoholic solution of strychnine, a sparingly soluble yellow precipitate of *strychnine dibromide*,

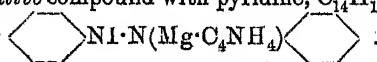


is obtained, which carbonises when heated, loses its colour in boiling alcohol, and dissolves incompletely in hot water. The addition of alkali to the aqueous filtrate precipitates a colourless, soluble basic bromide,  $\text{C}_{21}\text{H}_{21}\text{O}_2\text{N}_2\text{Br}$ , m. p.  $250^\circ$ , which, in alcoholic solution, yields with bromine in carbon disulphide solution a yellow substance, which appears to be a mixture of tri- and tetra-bromostrychnine.

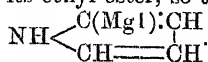
By the action of bromine in carbon disulphide on alcoholic brucine, a white, gelatinous precipitate is first formed, which redissolves by the further addition of bromine, the solution yielding a dark yellow precipitate. The white substance is a *bromobrucine*,  $\text{C}_{23}\text{H}_{25}\text{O}_4\text{N}_2\text{Br}$ , which differs from Laurent's bromobrucine in colour and in being reddened by mineral acids. The yellow precipitate is a non-hygroscopic *bromobrucine dibromide* (?),  $\text{C}_{23}\text{H}_{25}\text{O}_4\text{N}_2\text{Br}_2$ , different, therefore, from Beckurt's brucine tribromide.

C. S.

**Magnesium Pyrrol Iodide and its Use in the Synthesis of Pyrrole Derivatives.** BERNARDO ODDO (*Gazzetta*, 1909, 39, i, 649—659).—The action of pyrrole on magnesium methyl iodide in ethereal solution yields magnesium pyrrol iodide, which was separated in the form of its *additive* compound with pyridine,  $\text{C}_4\text{H}_4\text{N}_2\text{IMg}$  or



The action of carbon dioxide or ethyl chlorocarbonate on magnesium pyrrol iodide in ethereal solution yields pyrrole-2-carboxylic acid or its ethyl ester, so that magnesium pyrrol iodide has the constitution



T. H. P.

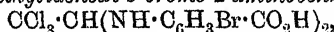
**Action of Potassium Hydroxide on Acetyl- $\psi$ -isatindioxime.** JEAN KOZAK (*Bull. Acad. sci. Cracow*, 1909, 628—632).—Acetyl- $\psi$ -isatindioxime is hydrolysed by 15% potassium hydroxide in two to three weeks at the ordinary temperature and in thirty minutes by heating, and yields the monoxime, not the expected dioxime. C. S.

**Quinaldyl Chloride.** EMIL BESTHORN (*Ber.*, 1909, 42, 2697—2698).—A final reply to Meyer and Turnau (this vol., i, 419). C. S.

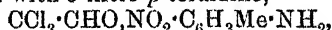
### Condensation of Chloral with Primary Aromatic Amines.

III. ALVIN S. WHEELER and STROUD JORDAN (*J. Amer. Chem. Soc.*, 1909, 31, 937—943).—In earlier papers (Abstr., 1903, i, 246; 1908, i, 392), descriptions have been given of the condensation products of chloral with several primary arylamines. The work has been continued, and the following compounds are described.

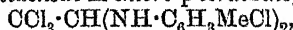
*Trichloroethylidenedi-m-bromoaniline*,  $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Br})_2$ , m. p. 115—116°, crystallises in colourless, rhombic bi-pyramids. *Trichloroethylidenedi-p-aminobenzoic acid*,  $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , m. p. 215—220° (decomp.), forms colourless crystals. *Trichloroethylidenedi-m-aminobenzoic acid*, m. p. 240° (decomp.), also forms colourless crystals. *Trichloroethylidenedi-5-bromo-2-aminobenzoic acid*,



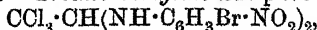
m. p. 174—175°, crystallises in clusters of needles. *Trichloroethylidenedi-o-nitro-p-toluidine*,  $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2)_2$ , m. p. 108—109°, forms a bright yellow, crystalline powder. An additive compound of chloral with o-nitro-p-toluidine,



m. p. 187—188°, has been obtained in the form of yellow needles. *Trichloroethylidenedi-p-nitro-o-toluidine*, m. p. 142—143°, forms long, golden-yellow needles. *Trichloroethylidenedi-m-nitro-p-toluidine*, m. p. 165—136°, crystallises in yellow needles, and is decomposed by boiling water. *Trichloroethylidenedi-m-chloro-p-toluidine*,



m. p. 110°, forms slender, white needles. The additive product of chloral with m-chloro-p-toluidine, m. p. 182—183°, crystallises in long, silvery white needles. *Trichloroethylidenedi-p-bromo-o-nitroaniline*,



m. p. 190—191°, forms small, lemon-yellow needles, and reacts with bromine to form a yellow, crystalline compound, m. p. 130—131°; the additive compound,  $\text{CCl}_3\cdot\text{CHO}\cdot\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{NH}_2$ , m. p. 232—233° (decomp.), crystallises in yellow needles. *Trichloroethylidenedi-p-bromo-m-nitroaniline*, m. p. 147—148°, also forms yellow needles. *Trichloroethylidenedi-p-iodoaniline*,  $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{C}_6\text{H}_4\text{I})_2$ , m. p. 123°, forms a

mass of steel-grey, branching needles. *Trichloroethylidenedi-4-bromo-1-naphthylamine*,  $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_{10}\text{H}_6\text{Br})_2$ , crystallises with one mol. of toluene. *Trichloroethylidenedi-p-aminoacetophenone*,  
 $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COMe})_2$ ,

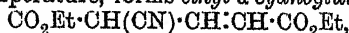
m. p. 162°, forms colourless plates.

Each of these condensation products is decomposed by strong mineral acids with regeneration of the amine. When the compounds are treated with a solution of bromine in glacial acetic acid, chloral is produced, together with the hydrobromide of the original amine or a bromoamine.

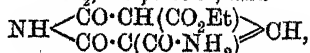
E. G.

**Constitution of the Imino-compounds from Ethyl Ethoxycoumalindicarboxylate and Ammonia or Alkylamines.** MAX GUTHZEIT and HERMANN EYSEN (*J. pr. Chem.*, 1909, [ii], 80, 34—68).

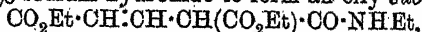
—The compound, m. p. 178°, obtained by the action of dry ammonia on a 5% benzene solution of ethyl 6-ethoxycoumalin-3:5-dicarboxylate, and formerly regarded as ethyl 2-hydroxy-5:6-dihydro-6-pyridone-3:5-dicarboxylate—easily changing to ethyl 2:6-dihydroxypyridine-3:5-dicarboxylate, m. p. 199° (Guthzeit, *Abstr.*, 1894, i, 71)—is now regarded, in consequence of the present work, as ethyl 6-imino-5:6-dihydrocoumalin-3:5-dicarboxylate, a constitution first suggested by Errera (*Abstr.*, 1902, i, 115) by reason of the analogous behaviour of ethyl 6-imino-5:6-dihydrocoumalin-3:4:5-tricarboxylate, which readily changes to the dihydroxypyridinetricarboxylate. Similar constitutions are assigned to the compounds obtained by the action of ethylamine or aniline on ethyl 6-ethoxycoumalin-3:5-dicarboxylate, m. p. 123° and 147° respectively (Guthzeit, Haussmann, and Band, *Abstr.*, 1895, i, 557, 560). The evidence for this change of opinion is mainly the action of sodium hydroxide, ammonium hydroxide, and ethylamine on the three compounds. 2*N*-Ammonium hydroxide, 0.5% sodium hydroxide, or 2% ethylamine, acting on the first-mentioned compound, m. p. 178°, at the ordinary temperature, forms *ethyl-α-cyanoglutaconate*,



a viscous, yellow oil with a bitter taste, which gives a red coloration with ferric chloride and forms a *sodium* derivative,  $\text{C}_{10}\text{H}_{13}\text{O}_4\text{NNa}$ , and an *ethyl* derivative,  $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$ , m. p. 79°. The same compound, m. p. 178°, reacts with 2.5% alcoholic ammonia to form the *amides*,  $\text{NH}_2 \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 170°, and



which decomposes at 259°, and reacts with ethereal 2.5% ethylamine to form the *substances*,  $\text{NH} \cdot \text{Et} \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 102°, and  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{Et}$ , an oil which readily yields diethylmalonamide, and with aniline to form compounds already described (Guthzeit, *Band, loc. cit.*). The compound  $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$ , m. p. 123°, obtained by the action of ethylamine on ethyl 6-ethoxycoumalin-3:5-dicarboxylate, reacts with 0.5% sodium hydroxide to form an oily *substance*,



and with 2.5% alcoholic ammonia to form Ruhemann and Morrell's amide,  $\text{NH}_2 \cdot \text{CH} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NH}_2$  (*Trans.*, 1891, 59, 743), a pyridine

derivative,  $\text{NEt} \begin{array}{c} \text{CO} \cdot \text{CH} (\text{CO}_2\text{Et}) \\ \text{CO} \cdot \text{C} (\text{CO} \cdot \text{NH}_2) \end{array} \text{CH}$ , m. p.  $204^\circ$ , and an oil which is probably  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHEt}$ . The compound  $\text{C}_{17}\text{H}_{17}\text{O}_6\text{N}$ , m. p.  $147^\circ$ , obtained by the action of aniline on ethyl 6-ethoxycoumalin-3 : 5-dicarboxylate, reacts with 0.5% sodium hydroxide to form the *anilide*,  $\text{CO}_2\text{Et} \cdot \text{C} (\text{CO}_2\text{Na}) : \text{CH} \cdot \text{CH} (\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NHPh}$ , from which the original compound is obtained by acidification, with dilute ammonium hydroxide to form an analogous ammonium salt,  $\text{C}_{17}\text{H}_{22}\text{O}_7\text{N}_2$ , with 2.5% alcoholic ammonia to form malonanilide and the pyridine derivative,  $\text{NPh} \begin{array}{c} \text{CO} \cdot \text{CH} (\text{CO}_2\text{Et}) \\ \text{CO} \cdot \text{C} (\text{CO} \cdot \text{NH}_2) \end{array} \text{CH}$ , m. p.  $271^\circ$ , and with ethereal 2.5% ethylamine to form diethylmalonamide,  $\text{CH}_2 (\text{CO} \cdot \text{NHEt})_2$ , and the *anilide*,  $\text{NHEt} \cdot \text{CH} : \text{C} (\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{NHPh}$ , m. p.  $84^\circ$ .

The formation of the preceding substances is explained by assigning to the compounds, m. p.  $178^\circ$ ,  $123^\circ$ , and  $147^\circ$ , the constitution  $\text{O} \begin{array}{c} \text{CO} \text{---} \text{C} (\text{CO}_2\text{Et}) \\ \text{C} (\text{NR}) \cdot \text{CH} (\text{CO}_2\text{Et}) \end{array} \text{CH}$ , where R is H, Et, and Ph respectively.

C. S.

**Action of Phenylhydrazine on Formaldehyde.** LEO F. ILJIN (*Ber.*, 1909, 42, 2886—2889).—By adding phenylhydrazine dissolved in acetic acid to an aqueous suspension of paraformaldehyde and warming the thoroughly stirred mixture for a short time on a water-bath, a yellow, crystalline solid,  $\text{C}_{21}\text{H}_{24}\text{N}_6$ , was obtained, which, after purification, separated from chloroform in colourless, mother-of-pearl, glistening scales; this substance darkens at  $115^\circ$ , and has m. p.  $170\text{—}180^\circ$ . The alcoholic mother liquors yielded a second compound,  $\text{C}_{30}\text{H}_{32}\text{N}_8$ , which crystallises in slender, colourless needles darkening at  $160^\circ$ , m. p.  $180\text{—}185^\circ$ .

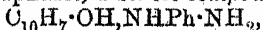
P. H.

**Compounds of Phenylhydrazine with Phenols.** ROBERTO CRUSA and A. BERNARDI (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 690—694).—The freezing-point curve of mixtures of phenol and phenylhydrazine exhibits (1) a minimum at  $18.06^\circ$ , which is the eutectic point for the system comprising phenol and the compound of phenol with phenylhydrazine, and (2) a maximum at about  $42^\circ$ , corresponding with the compound containing 1 mol. of phenol and 1 mol. of phenylhydrazine.

This compound,  $\text{Ph} \cdot \text{OH} \cdot \text{NHPh} \cdot \text{NH}_2$ , which may be prepared by mixing the fused constituents, crystallises from light petroleum in white needles, m. p.  $42^\circ$ , and when dissolved in benzene is largely dissociated into its components.

The compound,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{OH} \cdot \text{NHPh} \cdot \text{NH}_2$ , prepared from *m*-cresol and phenylhydrazine, crystallises from light petroleum in slender, white needles, m. p.  $36\text{—}37^\circ$ , and is strongly dissociated by benzene. The corresponding *p*-cresol compound,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{OH} \cdot \text{NHPh} \cdot \text{NH}_2$ , crystallises from light petroleum in white needles, m. p.  $26^\circ$ . *o*-Cresol also combines with phenylhydrazine, but the mixture remains superfused.

With  $\alpha$ -naphthol, phenylhydrazine gives an unstable compound, m. p.  $26^\circ$ , and with  $\beta$ -naphthol, a stable compound,



which crystallises from a mixture of benzene and light petroleum in white scales, m. p. 62—63°, and undergoes considerable dissociation when dissolved in benzene.

The compound,  $C_6H_4(OH)_2 \cdot 2NHPh \cdot NH_2$ , formed from catechol and phenylhydrazine, crystallises from benzene in white, silky needles, m. p. 63°. T. H. P.

**Phototropy of Certain Phenylhydrazones.** MAURICE PADOA (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 694—699. Compare Stobbe, *Abstr.*, 1908, ii, 339).—In order to throw light on the changes occurring in phototropic compounds under the influence of light, the author has studied the behaviour of crystalline mixtures composed of a phototropic substance and of a non-phototropic one capable of forming solid solutions with the former. In all the cases examined, such solid solutions exhibit behaviour differing from that of the pure phototropic substances.

In freezing benzaldehydephenylhydrazone—the molecular depression of freezing point of which is found to have the mean value  $K = 112.9$ —benzylidenebenzylamine has the mol. wt. 214.2—218.2, instead of 195. The pure phenylhydrazone colours rapidly in sunlight, and becomes decolorised only slowly in the dark, this latter change being favoured by heating. A mixture containing 4.6% of benzylidenebenzylamine becomes red in sunlight, but turns colourless again after an hour in the dark. With only 1% of the amine, the decoloration is almost complete in twenty-four hours. The pure phenylhydrazone, when heated slowly in diffused light, is completely decolorised at 115—120°, mixtures containing 1% and 3% of the amine at 95—100° and 80—85° respectively.

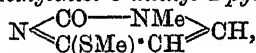
Mixed crystals of benzaldehydephenylhydrazone and diazoaminobenzene, containing 4.92% of the latter, are absolutely insensitive to light. A mixture containing 1.57% of the diazo-compound has its colour slightly intensified by the action of light, the reverse change being complete after twenty-four hours; if the action of light is repeated, the darkening is less than at first, and the decoloration correspondingly more rapid.

Anisaldehydephenylhydrazone becomes violet when exposed to light, but, if left exposed for a long time, again turns white, and does not again assume its property of colouring in the light even if kept for several days in the dark; its m. p. remains unchanged even after prolonged exposure. A mixture of this phenylhydrazone with anisylidenebenzylamine, containing 1% of the latter, when exposed to light, colours more intensely and more rapidly than the pure phenylhydrazone, and exhibits the same behaviour as the latter when the exposure is prolonged. The phenomena observed when the phenylhydrazone and mixtures of it with anisylidenebenzylamine are heated are similar to those shown by benzaldehydephenylhydrazone and its mixtures with benzylidenebenzylamine. A small proportion of benzaldehydephenylhydrazone is incapable of imparting phototropic properties to benzylidenebenzylamine. If compounds which do not form solid solutions with phototropic substances are fused with these, they exert no influence on the behaviour towards light.

*Anisylidenbenzylamine*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{CH}_2\text{Ph}$ , prepared by mixing anisaldehyde (1 mol.) and benzylamine (1 mol.), separates from light petroleum in white crystals, m. p.  $33^\circ$ . T. H. P.

**Pyrimidines. XLIII. Preparation of 3-Methyl- and 3-Benzyl-uracil.** HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1909, 42, 30—37).—In earlier papers (Abstr., 1907, i, 728; 1908, i, 692, 835, 1018; this vol., i, 59) accounts have been given of a study of the alkylation of 2-thiol-6-pyrimidones. Some irregularity has been observed in these reactions, analogous salts giving different results with the same halide, whilst with different halides the salt may be attacked in different positions. It has been considered of interest, therefore, to study the alkylation of some isomeric 6-thiol-2-pyrimidones. When 6-methylthiol-2-pyrimidone is treated with methyl iodide or benzyl chloride in presence of potassium hydroxide, 3 alkyl derivatives are produced; if isomeric products are formed in these reactions, the quantity is extremely small. The 6-thiol, like the 2-thiol, compounds are decomposed by hot hydrochloric acid, with formation of mercaptan and uracil derivatives. 3-Methyluracil has been thus obtained, and completes the series of the possible methyl-uracils.

6-Methylthiol-2-pyrimidone,  $\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{SMe}) \cdot \text{CH} \end{smallmatrix} \text{CH}$ , m. p.  $205^\circ$ , obtained by the action of methyl iodide on 6-thiouracil (Wheeler and Liddle, this vol., i, 61) in presence of sodium methoxide, forms long, slender needles or prisms. 6-Methylthiol-3-methyl-2-pyrimidone,



m. p.  $124^\circ$ , crystallises in needles.

3-Methyluracil,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{NMe} \\ \text{CO} \text{---} \text{CH} \end{smallmatrix} \text{CH}$ , m. p.  $232^\circ$ , crystallises in prisms; it dissolves in alkali hydroxide, and is reprecipitated on the addition of dilute hydrochloric acid. This compound does not colour a solution of diazobenzenesulphonic acid in sodium hydroxide, whereas 1-methyluracil gives a red coloration.

6-Methylthiol-3-benzyl-2-pyrimidone,  $\text{N} \begin{smallmatrix} \text{CO} \cdot \text{N}(\text{CH}_2\text{Ph}) \\ \text{C}(\text{SMe}) \text{---} \text{CH} \end{smallmatrix} \text{CH}$ , m. p.  $148\text{--}149^\circ$ , crystallises in prisms, and when boiled with hydrochloric acid is converted quantitatively into 3-benzyluracil (Johnson and Derby, Abstr., 1908, i, 1018).

A further study of the action of methyl iodide on the potassium salt of 2-ethylthiol-6-pyrimidone (Johnson and Heyl, Abstr., 1907, i, 728) has shown that both the 1- and 3-methyl derivatives are formed, whereas in the earlier work only the 1-methyl derivative was isolated.

E. G.

**Pyrimidines. XLIV. Preparation of 1:4-Dimethyluracil and of the Monobenzyl Derivatives of 4-Methyluracil.** HENRY L. WHEELER and DAVID F. MCFARLAND (*Amer. Chem. J.*, 1909, 42, 101—115).—An exceedingly convenient method for the preparation of 1:4-dimethyluracil is the following. Ethyl acetoacetate, thio-

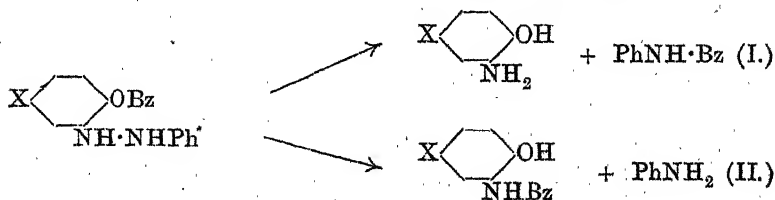
carbamide, and sodium ethoxide (2 mols.), when heated in alcoholic solution for thirty minutes, give an almost quantitative yield of 2-thio-4-methyluracil, which reacts with alcoholic potassium hydroxide and methyl iodide ( $> 3$  mols.) to form 2-methylthiol-1:4-dimethyldihydro-6-pyrimidone,  $\text{NMe} \cdot \text{C}(\text{SMe}) : \text{N} \begin{array}{c} \text{CO} \text{---} \text{CH} \text{---} \text{CMe} \end{array}$ , m. p.  $94^\circ$ , in 76.4% yield, which separates from water in silky needles, is volatile with steam, and is quantitatively changed to 1:4-dimethyluracil by boiling concentrated hydrochloric acid.

The reaction between 2-ethylthiol-4-methyldihydro-6-pyrimidone, alcoholic sodium ethoxide, and benzyl chloride yields 1-benzyl-2-ethylthiol-4-methyldihydro-6-pyrimidone,  $\text{C}_{14}\text{H}_{16}\text{ON}_2\text{S}$ , an oil which is converted by boiling hydrochloric acid into mercaptan, 4-methyluracil, and 1-benzyl-4-methyluracil,  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$ , m. p.  $194^\circ$ . Hagen's so-called 1-benzyl-4-methyluracil, m. p.  $233^\circ$ , is proved to be 3-benzyl-4-methyluracil by converting it and also 1:4-dimethyluracil into the same 3-benzyl-1:4-dimethyluracil, m. p.  $85\text{--}86^\circ$ , the former by methylation and the latter by benzylation. That the benzyl group is not in position 5 in the two preceding compounds, m. p.  $194^\circ$  and  $233^\circ$  respectively, is proved as follows. Ethyl benzylacetoacetate, thiocarbamide, and alcoholic sodium ethoxide yield ultimately 2-thio-5-benzyl-4-methyluracil,  $\text{C}_{12}\text{H}_{12}\text{ON}_2\text{S}$ , m. p.  $257\text{--}258^\circ$ , which is digested in alcohol with sodium ethoxide and ethyl bromide, whereby 2-ethylthiol-5-benzyl-4-methyldihydro-6-pyrimidone,  $\text{C}_{14}\text{H}_{16}\text{ON}_2\text{S}$ , m. p.  $166^\circ$ , is obtained, which is converted by hydrochloric acid into 5-benzyl-4-methyluracil, m. p.  $249\text{--}250^\circ$ .

1-Benzyl-3:4-dimethyluracil, m. p.  $164^\circ$ , is obtained by methylating 1-benzyl-4-methyluracil. The benzylation of 2-thio-5-benzyl-4-methyluracil yields 2-benzylthiol-5-benzyl-4-methyldihydro-6-pyrimidone,  $\text{CH}_2\text{Ph} \cdot \text{S} \cdot \text{C} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{N} \text{---} \text{CMe} \end{array} \text{C} \cdot \text{CH}_2\text{Ph}$ , m. p.  $194^\circ$ , which is very stable to hydrochloric acid, but is converted by hydrobromic acid into 5-benzyl-4-methyluracil. It is not immaterial, therefore, what mercaptan derivative is selected for desulphurisation of the preceding pyrimidines to uracil derivatives.

C. S.

**Reduction of Hydroxyazo-compounds.** HEINRICH GOLDSCHMIDT and MORITZ ECKARDT (*J. pr. Chem.*, 1909, [ii], 80, 135—149).—The paper contains little new work. It is known that the reduction of acylated o-hydroxyazo-compounds by zinc dust and acetic acid yields the hydrazo-compound (which may or may not be capable of isolation), which, by further reduction, may undergo fission, thus :



By experiments on benzeneazo- $\beta$ -naphthyl benzoate,  $\beta$ -benzeneazo- $\alpha$ -naphthyl benzoate, and benzeneazo-*p*-tolyl benzoate, the authors show that reduction proceeds mainly in direction (I) in alcoholic solution, and in direction (II) in acetic acid. Evidence is obtained in all cases that the reductive fission of the hydrazo-compound proceeds in a third direction, yielding an aminophenol (or naphthol), aniline, and benzoic acid. C. S.

**Quinazolines. XXII. 3-Amino-2-methyl-4-quinazolone and Certain of its Derivatives.** MARSTON TAYLOR BOGERT and ROSS A. GORTNER (*J. Amer. Chem. Soc.*, 1909, 31, 943—947).—In earlier papers (Abstr., 1906, i, 712, 988; 1908, i, 466) a description has been given of 5-, 6-, and 7-nitro-derivatives of 3-amino-2-methyl-4-quinazolone. The present communication deals with the preparation and properties of the parent substance.

When acetylanthranil is treated with hydrazine hydrate (50% solution), 3-amino-2-methyl-4-quinazolone,  $C_6H_4 \begin{smallmatrix} N=CHMe \\ | \\ CO-N \cdot NH_2 \end{smallmatrix} \cdot H_2O$ , is produced, which forms long, colourless needles, and, on heating at  $110^\circ$ , loses its water of crystallisation; the anhydrous compound melts at  $152^\circ$  (corr.). It does not yield azo-derivatives with aromatic nitroso-compounds, and is not oxidised by mercuric oxide. It condenses with ethyl diacetylsuccinate to form a pyrrole derivative. It gives a phenylcarbamino-compound with phenylcarbimide, and does not condense with ketones. When the quinazolone is treated with nitrous acid, it does not undergo diazotisation, but the amino-group is replaced by hydrogen. It is evident that an intermediate substance is produced, however, since, if after the addition of the nitrous acid the mixture is immediately poured into an alkaline solution of  $\beta$ -naphthol, a compound,  $C_{41}H_{32}O_8N_5$ , is produced, which forms bright red needles, darkens at  $200$ — $230^\circ$ , decomposes at  $266^\circ$  (corr.), and possesses high tinctorial power. If  $\alpha$ -naphthol is used instead of  $\beta$ -naphthol, a similar compound, m. p.  $245^\circ$  (decomp.), is produced. In one experiment with  $\beta$ -naphthol, however, the dye was not produced, but an additive compound,  $C_9H_8ON_3 \cdot C_{10}H_8O$ , m. p.  $144$ — $145^\circ$  (corr.), was obtained, which formed bright orange needles and did not exhibit tinctorial properties.

3-Amino-2-methyl-4-quinazolone hydrochloride, m. p.  $206.9^\circ$  (corr.), forms long, colourless needles. The picrate blackens at  $187^\circ$  (corr.). The formyl derivative softens at  $185^\circ$  and melts at  $203$ — $204^\circ$  (corr.). The acetyl derivative melts at  $176.5^\circ$  (corr.). 3-Phenylcarbamido-2-

methyl-4-quinazolone,  $C_6H_4 \begin{smallmatrix} N=CHMe \\ | \\ CO-N \cdot NH \cdot CO \cdot NHPh \end{smallmatrix}$ , does not melt below  $300^\circ$ . 3-Benzylideneamino-2-methyl-4-quinazolone,  $C_{16}H_{13}ON_3$ , forms stellate groups of needles, m. p.  $183^\circ$  (corr.).

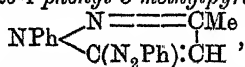
When acetylanthranil is warmed with *as*-phenylmethylhydrazine, a compound, m. p.  $106^\circ$  (uncorr.), is produced, which contains 9.90% of nitrogen. Hydrazine hydrate reacts with *m*-nitrobenzoylanthranil with formation of a compound, m. p.  $196$ — $197^\circ$  (decomp.). E. G.

**Phenylhydrazinopyrine and 5-Benzeneazo-1-phenyl-3-methylpyrazole.** AUGUST MICHAELIS and KARL ROBERT (*Ber.*, 1909, 42, 2765—2770).—The authors find that phenylhydrazine condenses with antipyrine chloride to form the phenylhydrazino-derivative, which is readily oxidised to benzeneazophenylmethylpyrazole. *Phenylhydrazinopyrine*,  $\text{NPh} \begin{array}{c} \text{NMe}=\text{CMe} \\ | \\ \text{N} \cdot \text{NHPH} \\ | \\ \text{C}=\text{CH} \end{array}$  or  $\text{NPh} \begin{array}{c} \text{NMe} \text{---} \text{CMe} \\ | \\ \text{C}(\text{N} \cdot \text{NHPH}) \cdot \text{CH} \end{array}$ , prepared

by heating phenylhydrazine and antipyrine chloride for some hours on the water-bath, is a yellow, viscid oil, which becomes black on exposure to the air; the *hydriodide* crystallises in yellow leaflets, m. p. 175°, and the *hydrochloride*, *platinichloride*, m. p. 161°, *ferrocyanide*, and *methiodide*, white leaflets, m. p. 201°, are described. *Phenylmethylhydrazinopyrine*,

$\text{NPh} \begin{array}{c} \text{NMe}=\text{CMe} \\ | \\ \text{N} \cdot \text{NMePh} \\ | \\ \text{C}=\text{CH} \end{array}$  or  $\text{NPh} \begin{array}{c} \text{NMe} \text{---} \text{CMe} \\ | \\ \text{C}(\text{N} \cdot \text{NMePh}) \cdot \text{CH} \end{array}$ , similarly prepared

from phenylmethylhydrazine and antipyrine chloride, forms large, yellow crystals, m. p. 128°; the *platinichloride*, *picrate*, small, yellow leaflets, m. p. 114°, *ferrocyanide*, *chromate*, *methiodide*, white leaflets, m. p. 191°, *ethiodide*, white leaflets, m. p. 130°, and benzoyl chloride additive compound, are described. *Phenylethylhydrazinopyrine*,  $\text{C}_{19}\text{H}_{22}\text{N}_4$ , forms stumpy, yellow crystals, m. p. 78°, the *alkyliodides* are mentioned. *5-Benzeneazo-1-phenyl-3-methylpyrazole*,



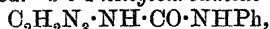
prepared by oxidising phenylhydrazinopyrine with yellow mercuric oxide, crystallises in yellowish-red needles, m. p. 62°; the *methochloride* was isolated as its *platinichloride*, m. p. 266—207°, and the *methiodide* crystallises in slender, yellow needles, m. p. 194°. J. C. C.

**The Amino-group of 1-Amino-1:3:4-triazole.** CARL BÜLOW (*Ber.*, 1909, 42, 2715—2721).—The author has already shown that 1-amino-1:3:4-triazole undergoes the three typical reactions for heterocyclic *N*-amino-substituted compounds, namely, that (1) the amino-group is displaced by hydrogen by the action of nitrous acid; (2) the basic character is greatly diminished as the salts are completely hydrolytically dissociated by water, and (3) with benzaldehyde a benzylidene derivative is obtained; these reactions were first shown to be applicable to the instance of an *N*-amino-substituted heterocyclic compound, namely, aminophenylthiodihydroiminazole,

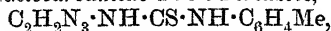
$\text{NPh} \begin{array}{c} \text{CH}:\text{CH} \\ | \\ \text{CS}-\text{N} \cdot \text{NH}_2 \end{array}$ , by Fischer and Hunsalz (*Abstr.*, 1894, i, 584). In

the present paper, further reactions are described which show that 1-amino-1:3:4-triazole behaves like an aromatic amine. *1-α-Phenylethylideneamino-1:3:4-triazole*,  $\text{CMePh} \cdot \text{N} \cdot \text{N} \begin{array}{c} \text{CH}:\text{N} \\ | \\ \text{CH}:\text{N} \end{array}$ , prepared by condensing 1-amino-1:3:4-triazole with acetophenone in alcoholic solution with the addition of a few drops of pyridine, forms yellow needles, m. p. 119°. *1-Formylamino-1:3:4-triazole*,  $\text{C}_2\text{H}_2\text{N}_3 \cdot \text{NH} \cdot \text{CHO}$ ,

prepared from the amine and formic acid, forms transparent, blunt crystals, m. p.  $117^{\circ}$ ; the *silver, copper, mercurous, and mercuric* compounds are described. *s*-1-Phenylcarbamido-1:3:4-triazole,



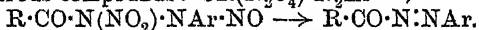
prepared from the base and phenylcarbimide, crystallises in small, slender, white needles, m. p.  $222^{\circ}$ ; when boiled with ferric chloride, a brown coloration is produced, and silver nitrate gives a milky turbidity. *s*-1-Tolylthiocarbamido-1:3:4-triazole,



prepared from the base and tolylthiocarbimide, forms white needles, m. p.  $156^{\circ}$ , then becoming solid, and again melting at  $194\text{--}196^{\circ}$ ; when boiled with ferric chloride, a brownish-yellow coloration is produced, and it is desulphurised by heating with silver nitrate.

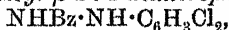
*s*-1-Naphthylcarbamido-1:3:4-triazole,  $\text{C}_2\text{H}_2\text{N}_3\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , similarly prepared, crystallises in soft, white, silky needles, m. p.  $240^{\circ}$ ; when boiled with ferric chloride, a yellowish-brown coloration is obtained, and silver nitrate gives a white precipitate. J. C. C.

**New Method of Preparing Acylazoaryl Compounds.** GIACOMO PONZIO (*Gazzetta*, 1909, 39, i, 661—666. Compare this vol., i, 443).—Acylazoaryl compounds may be prepared by treating the potassium salt of a primary dinitrohydrocarbon with the acetate of a diazo-compound, and, when a para-substituted diazo-derivative is employed, by dissolving the compound,  $\text{CR}(\text{N}_2\text{O}_4)\cdot\text{N}_2\text{Ar}$ , thus obtained in moist ether and removing the solvent by evaporation after nitrous fumes cease to be evolved. The diazo-salt of the dinitrohydrocarbon thus undergoes isomeric change into the corresponding acylarylnitro-nitrosohydrazine, which then loses 2 atoms of nitrogen and 3 of oxygen as nitrous compounds:  $\text{CR}(\text{N}_2\text{O}_4)\cdot\text{N}_2\text{Ar} \rightarrow$



In the case when moist ether transforms the diazo-salt into the isomeric stable azodinitrohydrocarbon,  $\text{CR}(\text{NO}_2)_2\cdot\text{N}\cdot\text{NAr}$ , it is necessary first to prepare, by means of anhydrous benzene, the nitro-nitrosohydrazine and subject this to the action of the ether.

*Benzoylazo-2:4-dichlorobenzene*,  $\text{NBz}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Cl}_2$ , prepared from 2:4-dichlorodiazobenzene acetate and the potassium derivative of  $\omega$ -dinitrotoluene, crystallises from light petroleum in flattened, brown needles, m. p.  $101^{\circ}$ , and is rapidly reduced by phenylhydrazine in ethereal solution to  $\alpha$ -benzoyl- $\beta$ -2:4-dichlorophenylhydrazine,



which crystallises from benzene in yellow needles, m. p.  $166^{\circ}$ .

*Bisbenzoylazodiphenyl*,  $\text{NBz}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NBz}$ , prepared from benzidine, crystallises from benzene in shining, yellowish-brown laminae, m. p.  $186\text{--}187^{\circ}$ . When reduced with phenylhydrazine in benzene solution, it is converted into *dibenzoyldiphenyldihydrazine*,  $\text{NHBz}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NHBz}$ , m. p.  $245^{\circ}$ . T. H. P.

**Transformations of Azo-compounds by means of Hydrogen Chloride in Alcoholic Solution.** PAUL JACOBSON (*Annalen*, 1909, 367, 304—331).—An investigation on the nature of the changes which azo-compounds undergo when treated with hydrogen chloride in methyl alcohol.

[With C. BARTSCH and A. STEINDRENCK.]—*Azobenzene and Hydrogen Chloride in Methyl Alcohol*.—Azobenzene is destroyed completely when its methyl-alcoholic solution is saturated with hydrogen chloride, kept for about twelve hours at the ordinary temperature, and subsequently boiled. The product of the reaction consists chiefly of benzidine, aniline, and *p*-chloroaniline, together with about 7–8% of a chlorinated amine,  $C_{12}H_8Cl_4N_2$ . The latter substance is 2:3:5:4'-tetrachloro-4-aminodiphenylamine, since it is produced by the chlorination of 4'-chloro-4-aminodiphenylamine, which is formed during the reaction; it is also formed by the action of hydrogen chloride on a solution of *o*-benzeneazotoluene in methyl alcohol; further, when oxidised it yields a tetrachlorobenzoquinonephenylimine, which is converted by sulphuric acid into *p*-chloroaniline and trichlorobenzoquinone.

The formation of the above compounds from azobenzene probably takes place through the following series of changes: (a)  $NPh:NPh + 2HCl = NPh:NHPh + Cl_2$ . (b)  $NPh:NPh + 4HCl = 2NH_2Ph + 2Cl_2$ . The hydrazobenzene passes into benzidine, whilst part of the aniline undergoes chlorination, yielding *p*-chloroaniline. (c)  $NPh:NPh + HCl = NPh:NHPh + Cl_2 \rightarrow NPh:NHPh + C_6H_4Cl$ . The *p*-chlorohydrazobenzene thus formed is converted by the combined action of the hydrogen chloride and of the chlorine liberated according to (a) and (b) into 2:3:5:4'-tetrachloro-4-aminodiphenylamine, most probably through the intermediate formation of 4'-chloro-4-aminodiphenylamine.

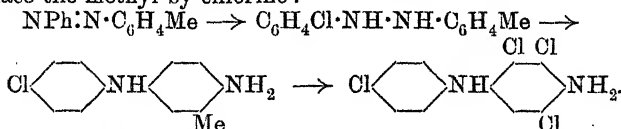
2:3:5:4'-Tetrachloro-4-aminodiphenylamine,  $C_{12}H_8N_2Cl_4$ , forms white, silky needles, m. p. 150–151°; the *o*-hydroxybenzylidene derivative,  $C_{19}H_{12}ON_2Cl_4$ , forms yellow crystals, m. p. 153–154°. The base is oxidised by chromic acid, yielding 2:3:5-trichlorobenzoquinone-*p*-chlorophenylimine,  $C_6H_4Cl:N:Cl < \begin{smallmatrix} OH=CO \\ CCl:CCI \end{smallmatrix} > CO$ , which crystallises in red needles, m. p. 153°, and is reduced by zinc dust and acetic acid to 2:3:5:4'-tetrachloro-4-hydroxydiphenylamine,  $C_{12}H_7ONCl_4$ , crystallising in rosettes of colourless needles, m. p. 128°.

[With A. LOEB.]—*p*-Chloroazobenzene, *p*-Chlorohydrazobenzene, and Hydrogen Chloride in Methyl Alcohol.—The reactions which occur when *p*-chloroazobenzene is treated in the same manner as azobenzene are analogous to those already described, the products formed being aniline, *p*-chloroaniline, and 2:3:5:4'-tetrachloro-4-aminodiphenylamine; since other chlorinated bases are not formed, however, it shows that a reaction analogous to (c) does not take place in this case. In two experiments, a substance,  $C_{12}H_{11}N_2Cl_2$ , either a dichlorodiaminodiphenyl or dichloroaminodiphenylamine, was isolated, but the conditions governing its formation could not be determined; it crystallises in slender, brown leaflets, m. p. 182–183°.

*p*-Chlorohydrazobenzene is converted by a cold saturated solution of hydrogen chloride in methyl alcohol into *p*-chloroazobenzene (37.5%), aniline and *p*-chloroaniline (15%), 5-chloro-2:4'-diaminodiphenyl (17.5%), 4-chloro-4'-aminodiphenylamine (2.5%), benzidine (0.5%), and 4-chloro-2'-aminodiphenylamine. In this case it is seen that an orthosemidine is formed together with the parasemidine, but chlorination does not enter into the various changes. The

same products, and to roughly the same extent, are formed by the action of a solution of sulphuric acid in methyl alcohol on *p*-chloro-hydrazobenzene.

[With C. BARTSCH.]—*Methylazobenzenes and Hydrogen Chloride in Methyl Alcohol*.—*m*-Benzeneazotoluene undergoes transformation with the same ease as azobenzene, but the ortho- and para-isomerides are far more stable. An exact separation of the compounds formed during the reaction has been effected only in the case of *o*-benzeneazotoluene; here, in addition to *o*-methylbenzidine, *o*-toluidine, and volatile chlorinated amines, the same tetrachloro-*p*-aminodiphenylamine was obtained as from azobenzene. Its formation shows that the chlorinating action of the hydrogen chloride which appears during the reaction is sufficient to replace the methyl by chlorine:



[With A. STEINBRECK.]—*Azobenzenecarboxylic Acids and Hydrogen Chloride in Methyl Alcohol*.—Azobenzene-*o*-carboxylic acid yields methyl benzidine-3-carboxylate, *p*-chloroaniline, and small quantities of other bases.

*Azobenzene-m-carboxylic acid*,  $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2$ , prepared by oxidising *m*-benzeneazotoluene with sodium dichromate and glacial acetic acid, crystallises in pale red leaflets, m. p. 166—167°; the silver salt was analysed; the methyl ester, prepared from the silver salt and methyl iodide, forms yellow leaflets, m. p. 57—58°. The acid is converted by a methyl-alcoholic solution of hydrogen chloride into *p*-chloroaniline and a substance, which is probably a methyl ester of a chlorinated benzidinecarboxylic acid.

Azobenzene-*p*-carboxylic acid yields *p*-chloroaniline, and probably a methyl chloroazobenzenecarboxylate and a methyl azobenzenecarboxylate.

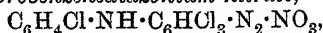
W. H. G.

**Diazonium Salts of Highly Halogenated Parasemidines and Certain other Highly Halogenated Bases.** PAUL JACOBSON (*Annalen*, 1909, 367, 332—347).—The polyhalogen derivatives of *p*-aminodiphenylamine when treated with sulphuric acid (50%) and excess of sodium nitrite do not yield diazonium sulphates, but diazonium nitrates, probably because the latter salts are soluble only with great difficulty. The diazonium nitrates are very stable towards mineral acids, and may be crystallised from hot concentrated nitric acid; on the other hand, they are decomposed by alcohol with great ease, the diazo-group being replaced by hydrogen.

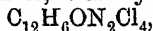
[With C. BARTSCH, A. LOEB, and A. STEINBRECK.]—*p*-Aminodiphenylamine is converted by a solution of bromine in glacial acetic acid at 0° into a tribromo-derivative,  $\text{C}_{12}\text{H}_7\text{N}_2\text{Br}_3$ , which crystallises in pale violet needles, m. p. 137—138°. A pentabromo-derivative,  $\text{C}_{12}\text{H}_7\text{N}_2\text{Br}_5$ , is formed by adding a solution of the base in glacial acetic acid to a solution of bromine in the same solvent at 80°; it forms bright red needles, m. p. 229—230°, and is converted by

sulphuric acid (50%) and sodium nitrite into the *diazonium nitrate*,  $C_{12}H_5NBr_5 \cdot N_2 \cdot NO_2 \cdot H_2O$ , crystallising in small, slender, yellow needles, m. p. 140—160° (decomp.). The latter substance, when boiled with alcohol, yields *pentabromodiphenylamine*,  $C_{12}H_5NBr_5$ , which crystallises in slender, white needles, m. p. 194—195°.

2:3:5:4'-Tetrachloro-4-aminodiphenylamine (compare preceding abstract), when diazotised in the same manner, yields 4-(p)-chloro-anilino-2:3:6-trichlorobenzene-diazonium nitrate,



which crystallises in yellow needles, and with alcohol yields 2:3:5:4'-tetrachlorodiphenylamine,  $C_{12}H_7NCl_4$ , small, colourless crystals, m. p. 107—108°; when decomposed by a smaller quantity of alcohol in the presence of potassium carbonate, it also yields a substance,



which crystallises in tufts of red needles, m. p. 176°, and is probably a nitroso-derivative of 2:3:5:4'-tetrachlorodiphenylamine.

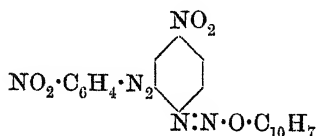
*Pentabromobenzene-diazonium nitrate*,  $C_6O_3N_3Br_5$ , prepared by diazotising pentabromoaniline in the presence of a large excess of sulphuric acid (50%), crystallises in white leaflets. Attempts to prepare a diazonium salt from tetrabromobenzidine by similar means were unsuccessful; when an alcoholic solution of the base is treated with gaseous nitrous acid, however, it yields *tetrabromodiphenylbis-diazonium hydrogen sulphate*,  $[C_6H_2Br_2 \cdot N_2 \cdot SO_4H]_2$ , which forms rod-like crystals, and is converted by alcohol into tetrabromodiphenyl (compare Trans., 1894, 65, 56).

W. H. G.

**Formation of p-Nitroaniline-Red.** MAURICE PRUD'HOMME and A. COLIN (*Bull. Soc. chim.*, 1909, [iv], 5, 779—785).—Cotton tissue when immersed first in a solution containing 25 grams of  $\beta$ -naphthol and 25 grams of sodium hydroxide solution (40°B) per litre, and then in a diazo-solution composed of 0.1 gram-molecule of p-nitroaniline, 0.1 gram-molecule of sodium nitrite, and 0.3 gram-molecule of hydrogen chloride per litre, is not coloured until washed in water, when it becomes orange-brown. If, however, the diazo-solution contains 0.2 gram-molecule of sodium acetate in addition to the above, thirty seconds' immersion of the cotton followed by immediate washing produces a good red colour, whilst with 0.5 gram-molecule of sodium acetate the cotton dyes a more bluish and intense red.

These differences, which are attributed by Goldschmidt, Lichtenstein, and others to differences in the concentration of the hydrogen ion, are considered by the authors to be due to the action of the ionised hydrogen chloride on the diazonium chloride, giving the two new electrolytes:  $(R \cdot NH^+ \cdot NCl) \cdot Cl^-$  and  $[R(NCl)_2]^+ \cdot H^-$  (R representing the  $NO_2 \cdot C_6H_4 \cdot$  group). These electrolytes are supposed to regenerate the diazonium chloride when the solution is diluted by the washing, and the naphthol then being in excess, produces a very pale red colour. Acetic acid being almost non-ionised, does not have this effect. The complex ions in the two electrolytes could be well expected to form foreign colouring matters with  $\beta$ -naphthol, and, in fact, the first of the above diazo-solutions when diluted and treated with sodium naphth-

oxide couples very slowly, giving first a brown precipitate and then an orange, insoluble colouring matter.



When the first diazo-solution is treated with increasing quantities (0.1, 0.2, and 0.3 gram-molecule) of sodium hydroxide, the red colour produced on cotton diminishes in intensity and disappears. If, however, the  $\beta$ -naphthol is previously precipitated on the cotton, the diazo-solution (containing 0.3 gram-molecule NaOH) gives an orange colour, possibly explained by the formation of the croceine-like compound (annexed formula).

E. H.

**Constitution of Protein.** EDUARD PFLÜGER (*Pflüger's Archiv*, 1909, 129, 99—102).—It is doubted whether the work of Fischer, Abderhalden, and others brings us much nearer to a solution of the question of the constitution of protein. In their work a large portion of the molecule is still unaccounted for. The only certain test for a protein is its capacity to maintain life and enter into the composition of protoplasm. If this definition is accepted, gelatin, protamines, and polypeptides are not proteins.

W. D. H.

**Hydrolysis of Proteins by Hydrogen Fluoride: New Results.** LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1909, 149, 41—43. Compare *Abstr.*, 1908, i, 706; this vol., i, 195).—Fifteen % aqueous hydrogen fluoride brings about complete hydrolysis of gelatin. The 20—30% acid gives amino-acids accompanied by dipeptides and tripeptides, whilst the 35% acid gives more complex polypeptides, one of which, on further hydrolysis, has yielded arginine, lysine, alanine, phenylalanine, and glycine. Acid containing 45% hydrogen fluoride furnishes the diamines only. The peptides obtained by means of this reagent are not of synthetic origin, since it is found that no condensation takes place when free amino-acids are heated alone with hydrogen fluoride. It follows, therefore, that the breakdown products of gelatin represent pre-existing natural complexes.

W. O. W.

**Casein and Paracasein.** T. KIKKOJI (*Zeitsch. physiol. Chem.*, 1909, 61, 139—146).—Löwenhardt's hypothesis that casein and paracasein (or, to adopt English nomenclature, caseinogen and casein) are identical is not confirmed. Their solubilities are different, and the latter substance is not coagulable by rennet.

W. D. H.

**Action of Rennet or Calcium Paracaseinate.** M. VAN DAM (*Zeitsch. physiol. Chem.*, 1909, 61, 147—163).—The digestion of paracasein (casein in English nomenclature) by rennet is accelerated by the number of hydrogen ions in solution. Petry's supposition that there is in rennet a special proteolytic enzyme acting only on casein was not confirmed. The peptic and rennetic activities of preparations of rennet run parallel, and this is in favour of the identity of pepsin.

and rennet. Sodium chloride hastens both actions. The action of the enzyme plays a part in the ripening of cheese. W. D. H.

**Yeast Nucleic Acid. II.** PHIBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 2703—2706).—The hydrolysis of yeast nucleic acid under carefully defined conditions (this vol., i, 620) yields a number of nucleosides (that is, complexes of a base and a carbohydrate), of which one, guanosin, has been already isolated. The mother liquor is treated with 25% lead acetate, and, after filtration, the soluble lead compounds of the nucleosides are precipitated by ammonium hydroxide. The precipitate is suspended in water, freed from lead by hydrogen sulphide, and the solution, after being evaporated to a syrup, is treated with a hot saturated solution of picric acid, whereby *adenosin picrate*,  $C_{10}H_{13}O_4N_5 \cdot C_6H_3O_7N_3$ , is obtained. It crystallises in glistening leaflets, and shrivels at  $185^\circ$  (corr.). *Adenosin*,  $C_{10}H_{13}O_4N_5$ , m. p.  $229^\circ$  (corr.), separates from hot water in long needles containing  $1\frac{1}{2}H_2O$ , has  $[\alpha]_D -67.30^\circ$  in *N*/10-sodium hydroxide, and yields adenine and *d*-ribose on hydrolysis with hot dilute sulphuric acid.

C. S.

**The Pentose from Inosic Acid and from the Pancreas.** CARL NEUBERG (*Ber.*, 1909, 42, 2806—2809).—The author recounts the different views as to the constitution of the pentose obtained from inosic acid, which has been identified as *d*-lyxose by Haiser and Wenzel (this vol., i, 540), and claimed as *d*-ribose by Levene and Jacobs (this vol., i, 541), identical with the pentose obtained from the guanylic acid of the pancreas (this vol., i, 620).

C. S.

**Systematic Investigation of the Oxydases. III.** OCTAVE DONY-HÉNAULT (*Bull. Acad. roy. Belg.*, 1909, 342—409. Compare Abstr., 1907, i, 1100; 1908, i, 588).—The doubtful nature of the guaiacum reaction as a test for the oxydases has been pointed out by Pighini (*Arch. Fisiol.* [iv], 1, 57), Lesser (Abstr., 1907, ii, 827), and Fouard (Abstr., 1906, i, 421). Experiments described in the paper show that freshly prepared tincture of guaiacum is extremely sensitive to alkali, being coloured yellow or green by quantities too small to be detected by the usual indicators. Tincture of guaiacum, when treated with small quantities of manganous acetate and then with traces of alkali, gives the characteristic blue colour. This reaction is prevented by small quantities of acid. An artificial laccase, obtained by precipitating with alcohol a mixture of gum arabic, sodium carbonate, and manganous formate, is only slightly active towards guaiacum, but if Rochelle salt (which acts by preventing the precipitation of the manganese by the alkali) is added before precipitation, a laccase as active as that from Japanese lac is obtained. These observations indicate that the guaiacum reaction, like the oxidation of quinol, is not characteristic of the oxydases. Since guaiacum is coloured blue by acid ferric chloride solution (although excess of the acid retards the reaction), it seems that the oxidation of this substance can be effected in both alkaline and acid solution.

In the previous paper it was stated that the oxidation of guaiacol is

not to be explained by the activity of the alkaline or the manganous elements of laccase. It is now shown that, although the coloration of guaiacol by ferric chloride is evanescent, addition of a very small quantity of alkali causes a red coloration, followed by a precipitate of tetraguaiacoquinone, the phenomena being in every way analogous to those observed by Bertrand with laccase (Abstr., 1904, i, 157). Moreover, the presence of manganese salts has no similar effect. The presence of acid renders the ferric chloride quite inactive, whilst the second coloration (with alkali), but not the first (evanescent), is only produced in the presence of oxygen. Some specimens of guaiacol do not give the reaction either with ferric chloride and alkali or with Bertrand's laccase. The conclusion is drawn that the guaiacol reaction, also, must be rejected as a test for oxydases. The coloration of guaiacol solution in the presence of hydrogen peroxide by milk, hitherto attributed to oxidising enzymes in the latter, is probably to be explained by the action of traces of iron and alkali in the milk.

Bertrand's laccase, although considerably more stable towards heat than the hydrolytic enzymes (invertase, pepsin, etc.), is rendered inactive by prolonged boiling. This can be completely explained by the production of a trace of acid during boiling, and experiments are described showing that, although the simple synthetic laccase obtained by alcoholic precipitation of a mixture of gum, manganous salt, and alkali is insensitive to heat, synthetic laccases containing ammonium chloride, the copper salt of asparagine, egg-albumin, or serum-albumin are rendered very much less active by boiling.

The inhibition by acid of both the guaiacum and the guaiacol reactions with artificial laccase indicates that the sensitiveness of Bertrand's laccase towards acids is to be explained simply by the neutralising action of the latter.

Thus all the typical properties of laccase can be reproduced by the catalytic association of manganous and ferric molecules with free alkali. Bertrand's view that laccase is an easily hydrolysed compound of a manganous base with a weak acid is shown to be erroneous. Laccase probably does not exist in the latex of the lac tree, but is formed during the alcoholic precipitation.

In the second part of the paper the author puts forward the view that none of the oxydases are truly enzymic in character, but are inorganic catalysts in a colloidal substratum. It is suggested also that the activity of the hydrolytic enzymes bears a similar explanation, the accelerating influence of traces of acid on invertase, Hanriot's work showing the activity of iron in lipase (Abstr., 1901, ii, 562), and that of Tribot and Chrétien (this vol., i, 73, 346) attributing a similar rôle to magnesium in invertase, being cited in support of this view.

[With EDOUARD LEROY.]—Euler and Bolin's (Abstr., 1908, ii, 1021) observations concerning the oxidation of quinol by the catalyst ( $Mn \times OH$ ) confirm those of the author, but the statement that this oxidation can be effected in acid solution is erroneous, the mistake arising from the fact that phenolphthalein was used as indicator, of which the sensitiveness to alkalis is known to be small. The lucerne laccase prepared by Euler and Bolin is quite dissimilar from Bertrand's laccase, being inactive towards quinol until treated with manganous

salt, and the quantity of acid added to it by them, whilst making it acid to phenolphthalein, leaves it still alkaline to Förster's reagent. Euler and Bolin find that the addition of citrates, tartrates, gluconates, etc., to laccase accelerates its action on quinol, and seem to attribute this action to the formation of complex ions containing manganese. The present authors, however, consider the activity of these salts to be due partly to the alkali produced by their hydrolysis and partly to their rendering manganous hydrate soluble. It is shown experimentally that the activating effect of sodium citrate decreases with its alkalinity, and disappears at the point of true neutrality. Only the trisodium citrate is at all active. In the absence of manganous salt, salts such as Rochelle salt (which, although neutral to phenolphthalein, is alkaline to Förster's reagent) increase the oxidation of quinol by alkali.

The oxidising activity of a manganous salt plus a citrate is greater than the sum of the activities of the two separately, and since the co-operative effect is greatest for the ratio  $12\text{Mn}:1$  citrate molecule, it cannot be due to the formation of a complex manganese citrate. Moreover, the co-operative effect of manganous salt + citrate being nearly the same as that of manganous salt + alkali indicates that the two actions are of the same kind.

E. H.

**Malt Catalase and the Mineral Catalysts.** HENRI VAN LAER (*Bull. Soc. chim. Belg.*, 1909, 23, 293—296).—The catalytic power of malt (as measured by the volume of oxygen liberated from hydrogen peroxide during the first minute of the action) is increased by alkali, reaching a maximum when the liquid is neutral to phenolphthalein. If the alkalinity is reduced by making the solution neutral to methyl-orange, the catalytic power diminishes. Ground dry malt retains a certain amount of activity even after heating for two hours at  $125^{\circ}$ , and must be heated at  $200^{\circ}$  in order to destroy its activity towards hydrogen peroxide. The volume of oxygen evolved by the action of malt on hydrogen peroxide is reduced by the addition of an equal weight of the same malt previously heated, indicating that heating liberates a trace of acid. The reduction of the catalytic power of one malt by addition of another is probably due to extra acidity in the latter, whilst the progressive increase in the catalytic power of a barley during germination and its decrease on kilning are also to be explained by changes in the reaction of the medium surrounding the catalase rather than to a change in the quantity of the latter.

Magnesium salts have no effect on hydrogen peroxide until partly transformed into hydroxide by addition of alkali.

The activity of blood-charcoal, animal-charcoal, and spongy platinum is affected by traces of alkali and acid similarly to that of malt catalase. The only fundamental differences between the latter and mineral catalysts are that malt catalase is used up in the reaction and that it is destroyed by heat.

E. H.

## Organic Chemistry.

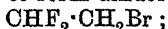
**A Mode of Production of Iodoform.** A. LABAT (*J. Pharm. Chim.*, 1909, [vi], 30, 107—109).—The supposed formation of iodoform from carbon dioxide recorded by Guérin (this vol., i, 126) depends on the ammonia employed, and does not occur with all specimens. It appears to be due to a ketonic impurity, probably acetone, which can be separated from the ammonia by neutralisation and distillation. The distillate gives the iodoform reaction, and forms an immediate white precipitate with Denigés' solution of mercuric sulphate. The samples of ammonia examined could not have contained more than 0.01% of the suspected impurity.

W. O. W.

**Preparation of Tetranitromethane.** R. SCHENCK (D.R.-P. 211198 and 211199).—Tetranitromethane was previously prepared by Pictet and Genequand (Abstr., 1903, i, 305, 596) by the action of acetic anhydride on diacetylorthonitric acid at 60°; the yield was 10% of the theory, and the action dangerously violent. It has now been found that a satisfactory yield can be obtained by slowly dropping acetic anhydride (120 parts) into a mixture of nitrogen pentoxide (155 parts) and nitrogen peroxide (75 parts) at a temperature below 40°.

F. M. G. M.

**Fluorodibromoethane and  $\alpha$ -Fluorobromoethylene.** FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1909, 728—743. Compare Abstr., 1898, i, 467; 1899, i, 254; 1902, i, 129).—It has been shown previously that antimony trifluoride condenses with tribromoethane in presence of bromine at 100° to form difluorobromoethane,



at higher temperatures some  $\alpha$ -fluoro- $\alpha\beta$ -dibromoethane,  $\text{CH}_2\text{Br} \cdot \text{CHBrF}$ , is also formed (Abstr., 1902, i, 129), and at 180° the amount of the latter obtained is twice as great as of the former. Further, at 180° a minute quantity of the isomeric  $\alpha$ -fluoro- $\beta\beta$ -dibromoethane,  $\text{CHBr}_2 \cdot \text{CH}_2\text{F}$ , is also produced. It follows from these observations that substitution of fluorine for bromine in the chain  $\cdot\text{CH}_2\text{Br}$  only occurs at the higher temperature.

Fluorobromoethylene reacts with hydrobromic acid (D 1.78) at 100° to form  $\alpha$ -fluoro- $\alpha\beta$ -dibromoethane, a small quantity of fluorotribromoethane being also produced, due probably to free bromine contained in the acid used.

$\alpha$ -Fluoro- $\alpha\beta$ -dibromoethane, on treatment with potassium hydroxide in alcohol, yields a mixture of two fluorobromoethylenes (compare Abstr., 1902, i, 129). The *s*-isomeride,  $\text{CHF} \cdot \text{CHBr}$ , b. p. 36°, is stable in air and does not polymerise. The *as*-isomeride,  $\text{CBrF} \cdot \text{CH}_2$ , b. p. 12.5°, oxidises rapidly in air, forming ethylene oxide, although the greater part of it polymerises spontaneously. It absorbs bromine

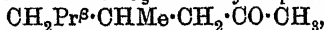
readily, yielding  $\alpha$ -fluoro- $\alpha\beta$ -tribromoethane, b. p.  $163^\circ$ , which can also be prepared by the substitution of fluorine in tetrabromoethane.

T. A. H.

**The Isolation of Aliphatic Alcohols.** CARL NEUBERG and E. KANSKY (*Biochem. Zeitsch.*, 1909, 20, 445—449).— $\alpha$ -Naphthylcarbimide is heated with an equimolecular proportion of the dry alcohol, and the resulting  $\alpha$ -naphthylcarbamate separated from a little dinaphthylcarbamide by extraction with light petroleum, from which the carbamate crystallises on cooling.  $\alpha$ -Naphthylcarbamates of the following alcohols were prepared: *n*-propyl, m. p.  $80^\circ$ ; isopropyl, m. p.  $105$ — $106^\circ$ ; *n*-butyl, m. p.  $71$ — $72^\circ$ ; isobutyl, m. p.  $103$ — $105^\circ$ ; sec-butyl, m. p.  $97$ — $98^\circ$ ; tert-butyl, m. p.  $100$ — $101^\circ$ ; isoamyl, m. p.  $67$ — $68^\circ$ ; optically active amyl, m. p.  $82^\circ$ ; sec-amyl, m. p.  $76$ — $79^\circ$ ; tert-amyl, m. p.  $71$ — $72^\circ$ ; *n*-heptyl, m. p.  $62^\circ$ ; *n*-octyl, m. p.  $66^\circ$ ; cetyl, m. p.  $81$ — $82^\circ$ ; allyl, m. p.  $109^\circ$ .

G. B.

**Condensation of isopropyl Alcohol with its Sodium Derivative.** Formation of Methylisobutylcarbinol and of  $\delta\zeta$ -Dimethylheptan- $\beta$ -ol. MARCEL GUERBET (*Compt. rend.*, 1909, 149, 129—132; *J. Pharm. Chim.*, 1909, [vi], 30, 153—161. Compare Abstr., 1902, i, 130, 583, 657; 1908, i, 162, 635).—The study of the reaction between alcohols and their sodium derivatives has now been extended to secondary aliphatic alcohols. When sodium is heated with excess of isopropyl alcohol for twenty-four hours at  $200^\circ$ , methylisobutylcarbinol is formed, together with  $\delta\zeta$ -dimethylheptan- $\beta$ -ol,  $\text{CH}_3\text{Pr}^\beta\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ . This substance, which arises from the condensation of sodium isopropoxide with methylisobutylcarbinol, is a liquid with a rose-like odour, b. p.  $194$ — $195^\circ$  (corr.),  $D_{20} 0.8787$ ; the acetyl derivative has b. p.  $201$ — $202^\circ$  (corr.). Oxidation with chromic acid mixture furnishes  $\delta\zeta$ -dimethylheptan- $\beta$ -one,



b. p.  $190$ — $191^\circ$ ,  $D_{20} 0.9024$ ; the semicarbazone has m. p.  $210^\circ$ . Oxidation of the ketone leads to formation of acetic acid and  $\alpha$ -dimethylvaleric acid, together with a little carbon dioxide and an acid,  $\text{C}_9\text{H}_{18}\text{O}_2$ .

W. O. W.

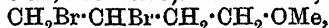
**Action of Active Copper on Linalool.** C. J. ENKLAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, 12, 104—108).—When linalool,  $\alpha_D - 17.14'$ , is passed at  $135^\circ$  over active copper, prepared by the reduction of the oxide at  $200^\circ$ , it is largely decomposed into hydrocarbon and water. By distillation, finally over sodium, the product yielded four fractions, three of which, b. p./12 mm.  $67.5$ — $68.5^\circ$ ,  $68.5$ — $69^\circ$ , and  $69$ — $70^\circ$ , assumed to be a single substance,  $\text{C}_{10}\text{H}_{18}$ , have been examined. The molecular refraction lies between those calculated for a monocyclic and an aliphatic terpene, whilst the molecular dispersion exceeds those of both. The substance rapidly absorbs two atoms of bromine, and a third very slowly with evolution of hydrogen bromide. Hydrogen at  $180^\circ$ , with nickel as catalyst, converts the substance into a product which yields a main fraction,  $\text{C}_{10}\text{H}_{18}$ , b. p.  $164$ — $166^\circ$ ,  $D_{20} 0.787$ , which is stable towards potassium

permanganate, but is attacked rapidly by bromine at the ordinary temperature. This behaviour is exhibited by the hydrocarbons,  $C_{10}H_{18}$ , obtained by the hydrogenation of dicyclic terpenes. The substance  $C_{10}H_{16}$  is oxidised by potassium permanganate to a glycol, probably  $C_{10}H_{18}O_2$ , and various acids, among which a butyric acid is present, and also a non-volatile acid, which is oxidised to a hydroxy-acid by hydrogen peroxide.

It appears, therefore, that linalool is dehydrated by active copper with closure of the ring.

Another method, in which closure of the ring is avoided as much as possible, consists in heating linalool and phenylcarbimide (2 mols.) at 140—150°. Carbon dioxide is evolved, *s*-diphenylcarbamide crystallises out, whilst a hydrocarbon is obtained by distillation, which has  $D_0^{20}$  0.810, and resembles myrcene in its odour and in its reduction by sodium and alcohol to a hydrocarbon having the b. p. of dihydro-myrcene.

Some Derivatives of  $\alpha\beta\delta$ -Trihydroxybutane. PARISELLE (*Compt. rend.*, 1909, 149, 295—298).—The ether,



prepared by Lespieau (*Abstr.*, 1907, i, 580), has b. p. 96°/16 mm.,  $n_D^{20}$  1.5158. When boiled with water and the resultant syrup fractionally distilled in a vacuum, two compounds are obtained: (1)

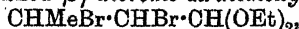
3-hydroxytetrahydrofuran,  $O \begin{array}{c} \diagup CH_2 \cdot CH \cdot OH \\ \diagdown CH_2 \cdot CH_2 \end{array}$ , b. p. 81—82°/13 mm.,

or 181° under ordinary pressure; its *phenylurethane* has m. p. 120°; (2)  $\alpha\beta$ -dihydroxy- $\delta$ -methoxybutane,  $OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot OMe$ , b. p. 121°/12 mm.,  $D^{20}$  1.11,  $n_D^{20}$  1.448; its *diphenylurethane* has m. p. 111—112°. When saturated with hydrogen bromide at 110—115°, it yields  $\alpha\delta$ -dibromo- $\beta$ -hydroxybutane,  $CH_2Br \cdot CH(OH) \cdot CH_2 \cdot CH_2Br$ , b. p. 114—115°/13 mm.,  $D^{20}$  1.2023,  $n_D^{20}$  1.544. When this is treated with potassium hydroxide in dry ether, it forms  $\alpha$ -bromo- $\Delta^7$ -butylene oxide,

$\begin{array}{c} CH_2 \\ | \\ O \end{array} \begin{array}{c} \diagup CH \cdot CH_2 \cdot CH_2Br \\ \diagdown \end{array}$ , b. p. 58°/14 mm., 160° under ordinary pressure,  $D^{20}$  1.59,  $n_D^{20}$  1.478; on boiling with water containing a little sulphuric acid the expected monobromohydrin was not formed, hydroxytetrahydrofuran being produced, together with some  $\alpha\delta$ -dibromo- $\beta$ -hydroxybutane, arising from fixation of hydrogen bromide by the unhydrolysed oxide.

W. O. W.

Ethyl Acetal of Tetrolaldehyde [Diethoxybutinene]. P. L. VIGUIER (*Compt. rend.*, 1909, 149, 403—405).—The following compounds were obtained in an unsuccessful attempt to prepare tetrolaldehyde from crotonaldehyde. The latter compound was converted into  $\alpha\beta$ -dibromobutaldehyde, which, on treatment by Claisen's method, readily furnished  $\beta\gamma$ -dibromo- $\alpha\alpha$ -diethoxybutane,



b. p. 113—114°/13 mm. On treatment with alcoholic sodium ethoxide this yielded bromo- $\alpha\alpha$ -diethoxybutinene,  $C_8H_4Br \cdot CH(OEt)_2$ , b. p. 86°/15 mm.,  $D_0^{20}$  1.247,  $D^{21}$  1.2255,  $n_D^{20}$  1.4565. Acid hydrolysis converted it into bromocrotonaldehyde,  $C_8H_4Br \cdot CHO$ , a pale yellow liquid, b. p.

63—64°/14 mm., having a penetrating odour, and forming crystalline derivatives with hydroxylamine and semicarbazide.

When bromo- $\alpha$ -diethoxybutinene is distilled with potassium hydroxide, a small quantity of *diethoxybutinene*,  $\text{CMe}:\text{C}\cdot\text{CH}(\text{OEt})_2$ , is obtained as an agreeably-smelling liquid, b. p. 62—65°/15 mm., 163—166° under ordinary pressure,  $D_4^{20}$  0.915,  $D_4^{23}$  0.8945,  $n_D^{23}$  1.437.

Attempts to obtain definite products by hydrolysis with acids were unsuccessful. W. O. W.

**Preparation of Mixed Glycerol Esters.** VEZIO VENDER (D.R.-P. 209943).—Glycerol was heated at 150° with anhydrous oxalic acid, and the resulting mixture of glycerol and monoformin treated with nitrosulphuric acid. The resulting mixture of nitroglycerol (67%) and *dinitroformin* (33%) is a pale yellow oil,  $D_4^{25}$  1.57.

*Nitroacetin*, prepared from acetin by the same method, is a pale yellow oil,  $D_{15}$  1.45, insoluble in water, benzene, or carbon disulphide, but soluble in alcohol or acetone; it contains 12.5% of nitrogen.

F. M. G. M.

**Alcoholysis of Lecithin.** ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1909, 61, 210—214).—The difficulties arising from oxidation during the alcoholysis of oils containing unsaturated acids (compare Haller, Abstr., 1908, i, 123) may be obviated by the addition of tin or zinc to the mixture of oil and alcoholic solution of hydrogen chloride. Naturally the same device may be employed with advantage in the esterification of acids which readily undergo oxidation.

Lecithin from egg having the iodine value 62 (Hübl), when treated with a 2.5*N*-solution of hydrogen chloride in methyl alcohol, yields an ester, b. p. 218—250°/32 mm., having the iodine value 86.7 (Hübl). This increase in the iodine value, which was observed in most experiments, is not so great as is required by the formula generally assigned to lecithin. It is probable, therefore, that some part of the molecule, other than the unsaturated fatty acids, is concerned in the absorption of iodine by lecithin. W. H. G.

**Action of Finely-divided Metals on the Aliphatic Acid Anhydrides.** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1909, [iv], 5, 814—819. Compare this vol., i, 452).—When acetic anhydride vapour is passed over commercial zinc dust heated in a tube at 230—240°, zinc acetate is formed on the upper wall of the tube, a mixture of almost equal parts of acetone and acetaldehyde distils, the gases evolved consist of rather more than two volumes of carbon dioxide to one of hydrogen, and carbon is deposited on the zinc. These results are to be explained by (1) the action of zinc oxide, thus:  $\text{O}(\text{COMe})_2 + \text{ZnO} = \text{Zn}(\text{CO}_2\text{Me})_2$ , and (2) the catalytic action of the metallic zinc decomposing one part of the anhydride into acetone and carbon dioxide, thus:  $\text{O}(\text{COMe})_2 = \text{CO}_2 + \text{COMe}_2$  (a), and another part into the two residues  $\text{CH}_3\cdot\text{CO}\cdot$  and  $\text{CH}_3\cdot\text{CO}_2\cdot$ , the latter of which decomposes into carbon dioxide, carbon, and hydrogen, part of the hydrogen reducing the acetyl to acetaldehyde, thus:  $\text{O}(\text{COMe})_2 = \text{CO}_2 + \text{H}_2 + \text{C} + \text{CH}_3\cdot\text{CHO}$  (b). The slight excess of carbon dioxide is

explained by the partial decomposition of the zinc acetate into carbon dioxide, acetone, and zinc oxide.

Propionic anhydride is decomposed by zinc dust at  $240^{\circ}$ , giving carbon, carbon dioxide, hydrogen, propaldehyde, diethyl ketone, and zinc propionate, the decomposition proceeding according to reactions analogous to (a) and (b) above. Butyric, isobutyric, and isovaleric anhydrides behave quite similarly.

The above five anhydrides are decomposed by finely-divided cadmium (produced by reducing the oxide with hydrogen) into the corresponding symmetrical ketone and carbon dioxide, no secondary reactions being observed.

The vapour of acetic anhydride when passed over finely-divided nickel heated at  $200-220^{\circ}$  is decomposed into a mixture of carbon, carbon monoxide, hydrogen, and acetic acid, the latter containing traces of acetaldehyde. Evidently the anhydride is catalytically decomposed into the two groups  $\text{CH}_3\cdot\text{CO}_2\cdot$  and  $\text{CH}_3\cdot\text{CO}\cdot$ , the latter of which decomposes into carbon monoxide, hydrogen, and carbon, whilst part of the hydrogen combines with the  $\text{CH}_3\cdot\text{CO}_2\cdot$  group to form acetic acid:  $(\text{COMe})_2\text{O} = \text{C}_2\text{H}_4\text{O}_2 + \text{CO} + \text{H}_2 + \text{C}$ .

The behaviour of propionic, butyric, isobutyric, and isovaleric anhydrides is quite analogous, the corresponding olefine being formed in place of hydrogen. At a higher temperature ( $280-290^{\circ}$ ) the carbon monoxide is converted into carbon dioxide and carbon.

Finely-divided copper is much less active. A temperature of  $290-300^{\circ}$  is required to effect decomposition, and the products in all cases are hydrogen, carbon monoxide, a little carbon dioxide, carbon, the aliphatic acid, traces of the corresponding aldehyde and ketone, and unattacked anhydride. The main reaction is the same as that produced by nickel.

Porphyrised iron at  $300^{\circ}$  decomposes the acid anhydrides, forming carbon, carbon dioxide, hydrogen, and considerable quantities of the aldehyde and ketone. No carbon monoxide is produced. The decomposition of acetic anhydride is expressed by the equations  $\text{O}(\text{COMe})_2 = \text{COMe}_2 + \text{CO}_2$  and  $\text{O}(\text{COMe})_2 = \text{CH}_3\cdot\text{CHO} + \text{H}_2 + \text{CO}_2 + \text{C}$ .  
E. H.

**Preparation of Acid Chlorides and Anhydrides.** FARBERWERKE VORM MEISTER LUCIUS and BRÜNING (D.R.-P. 210805).—Acid anhydrides can be conveniently prepared by the action of sulphur dioxide (either in gas or liquid form) on the dry salts of the required acids; and by subsequent treatment with chlorine the acid chlorides are formed. A detailed account of the preparation of acetic anhydride, acetyl chloride, and of benzoyl chloride is given. F. M. G. M.

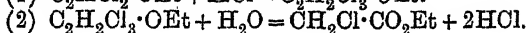
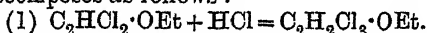
**Preparation of Formic Acid.** DAVID STRAUSS (D.R.-P. 209418).—Sodium formate in aqueous solution is treated with hydrofluoric acid (80%) and the free formic acid distilled off. The residual sodium fluoride is treated with lime, and the hydrofluoric acid recovered as its insoluble calcium salt. The substitution of hydrofluoric for sulphuric acid precludes the destructive action of the latter on the formic acid.

F. M. G. M.

**Replacement of Formic Acid by its Esters, especially as Concerns its Behaviour towards Bicarbonate Solutions.** O. MAKOWKA (*Zeitsch. angew. Chem.*, 1909, 22, 1601—1602).—For the decomposition of bicarbonate solutions formic acid may be replaced by such of its esters that are readily hydrolysed. Methyl and ethyl formates are not suitable. Glycol mono- and di-formates, as also mono-, di-, and tri-formin, react readily, but they possess the drawback that they are liquids. The mono- and di-formates of erythritol and mannitol, which are solids, are found to be satisfactory. It was not found possible to produce stable formates of mannitol of higher complexity than the diformate. It is probable that these higher formates are formed when mannitol is heated with excess of oxalic acid, but they immediately decompose with the formation of the diformate and formic acid; by distillation of the mixture under diminished pressure, concentrated and crystallisable formic acid is readily obtained.

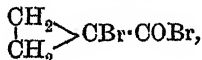
T. S. P.

**Production of Alkyl Chloroacetates from Dihalogenated Vinyl Ethers.** GEORGES IMBERT UND CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 210502. Compare this vol., i, 453).—It has previously been shown that concentrated hydrochloric acid produces this change. The reaction is now regarded as taking place in two phases, an additive product being first formed, which then decomposes as follows:



F. M. G. M.

**Bromination of cycloPropanecarboxylic Acid.** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 659—664).—The action of bromine on cyclopropanecarboxylic acid or its chloroanhydride leads to the formation of the bromoanhydride or chloroanhydride of  $\alpha$ -dibromobutyric acid. The normal bromination product,



is probably formed first, the action of the liberated hydrogen bromide on this compound resulting in the rupture of the cyclopropane ring.

*Ethyl  $\alpha$ -dibromobutyrate*,  $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO}_2\text{Et}$ , prepared by treating the chloro- or bromo-anhydride with alcohol in ethereal solution, is a heavy liquid with a fruity odour, b. p. 149—150°/52 mm.,  $D_4^{20}$  1.6871.

The action of zinc and alcohol on this ester does not yield ethyl cyclopropanecarboxylate, but results in reduction and hydrolysis of the ester, the main product of the reaction being zinc *n*-butyrate.

T. H. P.

**Electrolytic Preparation of Glyoxylic Acid.** KINZLBERGER & Co. (D.R.-P. 210693).—The electrolysis of ethyl oxanilate (5 parts) in 80% sulphuric acid (100 parts) with a mercury cathode leads to the formation of phenylglycine. At 5°, and employing a lead anode, the electrolysis of oxalic acid yields glyoxylic acid.

F. M. G. M.

**White and Yellow Silver Lævulates.** MARGARETE FURCHT and ADOLF LIEBEN (*Monatsh.*, 1909, 30, 555—634).—A white and a yellow modification of silver lævulate have long been known. In addition to Tollens' method, the white salt is obtained conveniently by adding to a solution of lævulic acid (1 part) in boiling water (200 parts) less than one equivalent of silver oxide, heating for the shortest time required for the solution of the oxide, and evaporating the filtered solution in a vacuum. The yellow salt is obtained by boiling 10 grams of lævulic acid in 600 grams of water with  $1\frac{1}{2}$  equivalents of silver oxide for six hours and cooling the hot filtered solution, whereby the nodular crystals of the yellow salt separate. When a moderately concentrated solution of the yellow salt is kept in a warm place for three months, it is decolorised, and the filtered solution yields by distillation in a vacuum a white salt, which, however, retains the crystalline appearance and shows the characteristic decomposition of the original yellow salt.

White silver lævulate is converted into the yellow form by prolonged heating with water, more rapidly in the presence of silver oxide. The yellow modification is changed into the white, with great loss of material, by heating its solution with animal charcoal at 70° for fifteen minutes, keeping overnight at the ordinary temperature, and evaporating the colourless filtered solution in a vacuum.

When the white salt is boiled with water, a portion is changed into the yellow salt and a portion undergoes decomposition, yielding silver, lævulic acid, and smaller quantities of carbon dioxide and a strongly odourous oil, which consists of, or contains, diacetyl, since it forms diacetyl dioxime with hydroxylamine. The boiling solution of the yellow salt decomposes more rapidly than that of the white salt, and yields the same products.

The decomposition of the white and the yellow salts by water increases with the temperature and with the time of heating. The rate of decomposition is greater the more finely divided the salt and the greater the surface of contact between the salt and the water, is increased by the presence of silver oxide, and is diminished by the presence of lævulic or succinic acid, sodium sulphate, or sodium nitrate.

A characteristic difference between the two salts is the following. Experiments on solutions containing from 20 to 1000 parts of water to 1 part of salt show that the decomposition of the white salt, effected by twenty-four hours' heating on a water-bath, is smaller the greater the quantity of water present, and that the deposited silver is always granular. Under similar conditions the decomposition of the yellow salt in solutions containing from 20 to 200 parts of water to 1 part of salt is more pronounced, but is again smaller the greater the amount of water present, and the deposit of silver is granular. When, however, a solution of 1 part of the yellow salt in 300—1000 parts of water is heated under the same conditions, an extraordinarily pronounced decomposition occurs, greater even than that of a solution of 1 part of salt in 20 parts of water, and the silver is obtained in colloidal suspension. The great decomposition in this case is due very probably to the large surface exposed by the colloidal silver.

Since white and yellow silver lævulates give the same products of decomposition, are interconvertible, form the same methyl lævulate with methyl iodide, and have the same solubility either separately or mixed, it appears very probable that they are one and the same substance, the colour and the characteristic properties of the yellow salt being due to a small amount of impurity. Attempts to isolate the impurity by extraction with various solvents have failed, but its presence has been proved by the following. A solution of the yellow salt is treated with the equivalent amount of hydrochloric acid, and the filtered solution, after being evaporated to a small bulk, is treated with ether, whereby the lævulic acid is extracted, leaving a small residue of an amorphous, brown substance, which is soluble in water (only sparingly soluble after being dried at  $100^{\circ}$ ) and, when added to a solution of the white silver lævulate, causes the salt to be deposited, after evaporation, in yellow, nodular crystals, and also increases very considerably its rate of decomposition by boiling water, the silver being obtained in a colloidal form if the solution is sufficiently dilute. The amorphous substance, which has reducing properties, does not exist apparently as such in the yellow salt, but is continually destroyed during the decomposition of the salt, yielding the odorous oil mentioned previously, and is continually being regenerated at the expense of the lævulic acid. At the ordinary temperature, daylight exerts on a solution of the white or yellow salt a decomposing influence very similar to that of heat, but in a very much smaller degree. There is a great difference, however, between the actions of light and heat. The former causes a deposition of silver from a solution of the yellow salt, but the salt remaining in solution becomes more stable, just as though the amorphous impurity, originally existent in the yellow salt, has been destroyed and is not being regenerated.

The decomposition of the white and yellow salts by boiling water under otherwise equal conditions is greater in a horizontal sealed glass tube than in a vertical sealed glass tube or in a sealed glass flask. The white and the yellow salts decompose to the extent of 19—23% and 41% respectively when a solution of one part of the salt in 20 parts of water is heated in a horizontal tube for twenty-four hours in boiling water.

C. S.

**Preparation of Magnesium Phosphotartrate.** KARL SORGER (D.R.-P. 210857).—*Magnesium phosphotartrate*, colourless powder or crystalline nodules, is obtained by the action of (1) magnesium hydrogen tartrate on magnesium phosphate; (2) magnesium hydrogen phosphate on neutral magnesium tartrate; or (3) the decomposition of sodium hydrogen phosphotartrate with magnesium oxide. It is not easily soluble in water or acids, but dissolves in ammonium hydroxide or dilute alkalis; it is decomposed by warm concentrated sulphuric acid with evolution of the oxides of carbon. Being tasteless, this salt should be of therapeutic value.

F. M. G. M.

**Preparation of an Allophanic Ester of Castor Oil.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 211197).—The *allophanic acid* ester,  $C_8H_5O_3(CO \cdot C_{17}H_{32} \cdot O \cdot C_2O_2N_2H_3)_8$ , colourless, tasteless,

odourless powder, m. p. 61—62°, is produced on adding carbamide hydrochloride to a solution of castor oil in benzene and boiling during one hour; it dissolves sparingly in cold, but readily in hot, alcohol, and is insoluble in water. F. M. G. M.

**Oxidation of Phoronic Acid by Nitric Acid.** RICHARD ANSCHÜTZ and PAUL WALTER (*Annalen*, 1909, 368, 95—100. Compare Anschütz, Abstr., 1893, i, 304).—When phoronic acid is heated with 50% nitric acid at 90° for about ten hours, it is converted into a mixture of approximately equal quantities of dimethylmalonic acid and *as*-dimethylsuccinic acid, the amount of these acids actually obtained being about 77% of that required by the equation:

$[\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}_2]_2\text{CO} \rightarrow \text{CMe}_2(\text{CO}_2\text{H})_2 + \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}.$   
The formula assigned previously (*loc. cit.*) to phoronic acid and given in the preceding equation is thus definitely established.

Attempts to prepare the substance  $\text{CO} \left\langle \begin{smallmatrix} \text{CH}_2\cdot\text{CMe}_2 \\ \text{CH}_2\cdot\text{CMe}_2 \end{smallmatrix} \right\rangle \text{CO}$  by the dry distillation of calcium phoronate were unsuccessful. W. H. G.

**Degradation of Cholic Acid. I. Fusion of Bilianic Acid with Potassium Hydroxide.** OTTO VON FÜRTH and ERNST JERUSALEM (*Biochem. Zeitsch.*, 1909, 20, 375—383).—The only product which could be isolated after fusion with potassium hydroxide at 220° was a minute quantity of unchanged bilianic acid. G. B.

**Degradation of Cholic Acid by Oxidation.** E. LETSCHE (*Zeitsch. physiol. Chem.*, 1909, 61, 215—239. Compare this vol., i, 587).—The formula assigned by Panzer to cholic acid (this vol., i, 586) is criticised adversely. The formation of bilianic acid from dehydrocholic acid points to the presence of an ethylene linking in the latter compound, and consequently also in cholic acid. Further, it is to be expected that the molecule of cholic acid having Panzer's formula would readily decompose into two roughly equal parts at the secondary alcohol group after its conversion into the ketonic group, but bilianic acid is very stable and yields cilianic acid when oxidised.

Cholic acid when acted on by a mixture of equal volumes of nitric acid (D 1.38) and sulphuric acid (D 1.84) yields a pentabasic acid,  $\text{C}_{19}\text{H}_{28}\text{O}_{10}$ , crystallising in slender prisms, m. p. 226° (decomp.),  $[\alpha]_D^{14} + 12.3^\circ$  (in 96% alcohol); it behaves as a saturated compound towards bromine and potassium permanganate, and when heated above its m. p. liberates 2 mols. of carbon dioxide. The silver,

$\text{C}_{19}\text{H}_{28}\text{O}_{10}\cdot\text{Ag}_5\cdot\text{H}_2\text{O}$ ,  
barium,  $(\text{C}_{19}\text{H}_{28}\text{O}_{10})_2\text{Ba}_3$ , and copper,  $(\text{C}_{19}\text{H}_{28}\text{O}_{10})_2\text{Cu}_5$ , salts are amorphous powders; other complex copper salts were also prepared and analysed. The diethyl ester,  $\text{C}_{23}\text{H}_{36}\text{O}_{10}$ , crystallises in very slender needles, m. p. 195—196°,  $[\alpha]_D^{20} + 11.39^\circ$  (in absolute alcohol); it loses carbon dioxide when heated above its m. p., and when boiled for one hour with a *N*/2-potassium hydroxide solution yields the double compound,  $\text{C}_{19}\text{H}_{28}\text{O}_{10}\cdot\text{C}_{21}\text{H}_{32}\text{O}_{10}$ , crystallising in stellate aggregates of slender needles, m. p. 207—208°,  $[\alpha]_D^{15} + 10.2^\circ$ . The following salts of the latter substance were analysed: silver,  $\text{C}_{40}\text{H}_{52}\text{O}_{20}\cdot\text{Ag}_8\cdot 2\text{H}_2\text{O}$ ; copper,  $\text{C}_{40}\text{H}_{52}\text{O}_{20}\cdot\text{Cu}_4\cdot 4\text{H}_2\text{O}$ ; iron,  $\text{C}_{19}\text{H}_{28}\text{O}_{10}\cdot\text{Fe}_2\cdot\text{C}_{21}\text{H}_{29}\text{O}_{10}$ .

The diethyl ester,  $C_{23}H_{36}O_{10}$ , when boiled with a  $N/2$ -potassium hydroxide for longer than one hour, yields an *acid*,  $C_{19}H_{28}O_{12}$ , crystallising in rhombic plates; it softens and froths up at about  $140^{\circ}$ , subsequently becomes solid, and then has m. p.  $230-231^{\circ}$ ; when heated at  $115^{\circ}$  it loses  $2H_2O$ , and at about  $125^{\circ}$  loses  $2\frac{1}{2}H_2O$ , yielding the *anhydride*,  $(C_{18}H_{27}O_8 \cdot CO)_2O$ , a white substance, m. p.  $230-231^{\circ}$ ; the *ammonium*,  $C_{19}H_{29}O_{12}(NH_4)_3$ , and *silver*,  $C_{19}H_{28}O_{12}Ag_4$ , salts were analysed. A tetrabasic *acid*,  $C_{18}H_{28}O_8$ , was sometimes obtained by boiling the ester,  $C_{23}H_{36}O_{10}$ , with  $N$ -potassium hydroxide solution; it crystallises in slender needles, commences to char at  $273^{\circ}$ , and is brownish-black at  $280^{\circ}$ ; the *diethyl ester*,  $C_{22}H_{30}O_8$ , forms stellate aggregates of lamellæ, m. p.  $248^{\circ}$ .

A *substance*,  $C_{48}H_{76}O_{10}$ , is formed together with the ester,  $C_{23}H_{36}O_{10}$ , during the esterification of the acid,  $C_{19}H_{28}O_{12}$ ; it forms spherical aggregates of slender crystals, m. p.  $183-184^{\circ}$ . W. H. G.

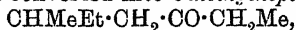
**Action of Iron and Cyanides on the Spontaneous Oxidation of Cystine.** Action of Metals and Strong Salt Solutions on the Spontaneous Oxidation of Cystine. ALBERT P. MATHEWS and SYDNEY WALKER (*J. Biol. Chem.*, 1909, 6, 289-298, 299-312).—Spontaneous oxidation of cystine occurs in alkaline solutions; the rate of this is increased by the addition of a mixture of ferric chloride and potassium cyanide, although neither reagent alone has any action. The products of oxidation and the mechanism of its acceleration are unknown.

The spontaneous oxidation of cystine to cystine is accelerated by a small amount of iron; some metals act in the same way, but others retard, and others again have no effect on the oxidation. An explanation, based on "solution tension," is given of the actions of different metals and their salts. W. D. H.

**A New Isomeride of Pinacolin.** F. CLAESSENS (*Bull. Soc. chim.*, 1909, [iv], 5, 809-812).—When pinacolyl bromide,  $CMe_3 \cdot CHMeBr$ , is boiled with powdered potassium hydroxide in a reflux apparatus for three hours and the fraction of the product b. p.  $57-65^{\circ}$  treated with iodine and mercuric oxide in the manner described previously (this vol., i, 127), an iodohydrin is formed, which, on pouring its ethereal solution on to an excess of solid potassium hydroxide, is transformed into a new *oxide*. This forms a colourless, agreeably smelling liquid, b. p.  $100.7-101.4^{\circ}$ ,  $D_4^{20}$  0.8413, which combines energetically with hydrogen chloride and bromide. When treated with an equal volume of water, the two liquids form a homogeneous product after several weeks, but with nine volumes of water, the oxide, although diminishing considerably in volume, does not disappear. A 10% solution of potassium hydroxide has apparently no action. If treated with an equal volume of water containing a trace of acid, the oxide diminishes in volume and thickens considerably. It is not reduced by sodium in moist ether. E. H.

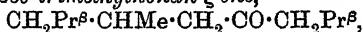
**Synthesis of Unsaturated Aliphatic Ketones.** F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1909, 149, 422-423. Compare Abstr., 1908, i, 854).—Propanone reacts energetically with calcium

carbide, forming mesityl oxide, isophorone, xylitone, and more complex compounds. Under the special conditions already described, mesityl oxide is the sole product. The ketone obtained previously by the action of calcium carbide on butanone is now shown to be  $\epsilon$ -methyl- $\Delta^2$ -hepten- $\gamma$ -one,  $\text{CH}_3\text{Me}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2\text{Me}$ ; it forms a semicarbazone, m. p. 114—115°, and on hydrogenation at 180° by Sabatier and Senderens' method is converted into  $\epsilon$ -methylheptan- $\gamma$ -one,



an agreeably smelling liquid, b. p. 153—155°/760 mm.,  $D^{24}_D$  0.820; the semicarbazone has m. p. 102°.

Calcium carbide acts on  $\beta$ -methylpentan- $\delta$ -one, furnishing  $\beta\delta\delta$ -trimethyl- $\Delta^2$ -nonen- $\zeta$ -one,  $\text{CH}_2\text{Pr}^\beta\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\text{Pr}^\beta$ , b. p. 217—219°/760 mm.,  $D^{18}_D$  0.838,  $n^{18}_D$  1.4491; the oxime is a viscous liquid, b. p. 143—145°/17 mm. On catalytic hydrogenation at 280°, the ketone yields  $\beta\delta\delta$ -trimethylnonan- $\zeta$ -one,



b. p. 210—212°/760 mm.,  $D^{18}_D$  0.820,  $n^{18}_D$  1.4262; the oxime has b. p. 138—140°/15 mm.

Mesityl oxide is attacked by calcium carbide with formation of a liquid,  $\text{C}_{12}\text{H}_{18}\text{O}_2$ , b. p. 238—242°/741 mm.,  $D^{17}_D$  0.937, having a penetrating odour. This probably consists of a mixture of ketones, since it gives two semicarbazones, one of which is gummy, whilst the other crystallises in prisms, m. p. 165—166°. On hydrogenation, it yields a liquid from which no definite compounds have been isolated.

W. O. W.

**Preparation of Ketonesulphoxylates.** FARBWERKE VORM. MEISTER, LUCIUS and BRÜNING (D.R.-P. 210467. Compare this vol., i, 455).—Zinc sulphite (145 parts) is suspended in water (1000 parts) and treated with acetone (65 parts) and zinc dust (120 parts), the whole being stirred during twenty hours at a temperature of 50—55°. The zinc is precipitated with sodium carbonate, and the filtrate consists of a solution of sodium acetonesulphoxylate.

The acetone may be replaced by methyl ethyl ketone, and the zinc sulphite by ammonium sulphite, when the reaction is complete in ten hours.

F. M. G. M.

**"Solubilisation" of Colloidal Starch by the Action of Alkalis.** EUGÈNE FOUARD (*Bull. Soc. chim.*, 1909, [iv], 5, 828—834).—The addition of alkalis to solutions of the various polysaccharides causes a progressive alteration in their optical rotatory power, usually explained by the gradual neutralisation of their acid groups, since definite chemical compounds are precipitated by addition of a large excess of alcohol. It has already been shown (this vol., i, 209) that the progressive "solubilisation" of colloidal starch by alkalis is accompanied by a corresponding change in the rotatory power of the solution.

The composition of the precipitates formed when mixtures of 20 c.c. of a clear solution of starch containing 25.79 grams per litre with 5 c.c. of solutions of potassium hydroxide, ammonia, or piperidine, of varying strength, are added to 250 c.c. of absolute alcohol, has been studied.

The precipitates obtained in the presence of potassium hydroxide continued to give up alkali when washed with alcohol, even when the washing had been prolonged over some months, and the amount of alkali precipitated with the starch was, therefore, determined indirectly by estimating that left in solution. The results of the experiments with potassium hydroxide show that as the amount of alkali present decreases from 3.287 grams to 0.0147 gram, that precipitated with the starch decreases from 0.169 gram to 0.0091 gram or from 0.946 to 0.0512 gram-molecule per gram-molecule of starch. By plotting the amounts of alkali fixed by 1 gram-molecule of starch (as ordinates) against the total numbers of gram-molecules of potassium hydroxide present (as abscissæ), a hyperbolic curve is obtained, showing that the absorption of alkali varies in a continuous manner. It is therefore proved that no chemical compound of starch and potassium hydroxide is formed.

If a colloidal starch solution is used in place of the clear solution, an analogous series of numbers is obtained, but for a given concentration of alkali, the amount carried down from the colloidal is invariably less than that from the clear starch solution.

The experiments with ammonia and piperidine give similar results, but the proportion of alkali absorbed by the starch is less in the case of ammonia than in the presence of potassium hydroxide, and still less with piperidine.

Observations of the conductivity of solutions of potassium hydroxide, ammonia, and piperidine, alone and after adding a clear starch solution, show that in all three cases ionisation is diminished by addition of the starch solution, whereas if compounds with the alkali were formed, it would be increased in the case of ammonia and piperidine.

The conclusion is drawn that the action of alkalis on starch in solution is one of "solubilisation," that is, of subdividing the granules of the colloid to a high degree, at the same time modifying them (by altering the optical rotatory power) and being fixed by them in a variable proportion. This extremely complex phenomenon is neither purely chemical nor purely physical, but is an intramolecular change.

E. H.

**Electric Transport of Glycogen and Starch.** FILIPPO BORTAZZI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 87—90).—The results of the author's experiments are not in accord with those of Hardy (Abstr., 1906, i, 121), according to whom glycogen and starch are relatively isoelectric hydrosols.

When solutions of glycogen and starch are subjected to a field of about 5 volts per cm. (0.1 milliampere), both the glycogen and starch move towards the anode, only traces migrating towards the cathode. In the presence of small proportions of mineral acids, alkalis, or neutral salts, glycogen loses its electronegative character and undergoes no migration in either direction. Starch, however, behaves like protein or gelatin; in acid solution it migrates towards the cathode and in alkaline solution towards the anode, whilst in presence of neutral salts no migration is observed.

Hardy's results (*loc. cit.*) were probably obtained with glycogen less

pure than that employed by the author, a trace of an electrolyte being sufficient to prevent transport. T. H. P.

**Lecithin-glucoses and Jecorin.** A. BASKOFF (*Zeitsch. physiol. Chem.*, 1909, 61, 426—453).—The lecithin-glucoses, which can be separated from one another by their solubilities, are unions (or only mixtures) of glucose with the cleavage products of lecithin, and are of very variable composition. Drechsel's jecorin is regarded as a similar material obtained from lecithin or other phosphatides. W. D. H.

**Etherifying Action of Organic Bases.** THÉODORE VAN HOVE (*Bull. Acad. roy. Belg.*, 1909, 759—772).—The author has shown that when a solution of quinoline hydrochloride in an alcohol is heated in a closed vessel, the corresponding alkyl ether is formed, and that the action is due to the hydrogen chloride liberated by the dissociation of the amine hydrochloride (Abstr., 1907, i, 173). Since the amount of dissociation in any given case must be proportional to the strength of the base, he has endeavoured to apply this method to the determination of the relative strengths of organic bases.

A semi-normal solution of the amine hydrochloride in sufficient 98.5% alcohol to form 20 c.c. was heated at 180° during two hours. From the resulting product 15 c.c. were distilled off with suitable precautions to avoid loss of ether, and the distillate was agitated with three times its volume of glycerol, a known and sufficient volume of ether being added to cause complete separation of the ether formed, from the alcohol-glycerol mixture. The separated ether was then measured. The results are not strictly quantitative, but afford qualitative indications of the relative strengths of bases.

The action of triamylamine hydrochloride on ethyl alcohol was examined in detail, with a view to determine the nature of the secondary reactions. The volatile products consisted of ethyl chloride, ethyl ether, and ethyl isoamyl ether, the first and third being formed only in small quantities. From the saline residue, ethyldiisoamylamine and diethylisoamylamine were obtained. T. A. H.

**Preparation of Guanidine.** CELSO ULPANI (D.R.-P. 209431).—When dicyanodiamide is treated with aqua regia, a quantitative yield of guanidine nitrate is obtained. One hundred grams of dicyanodiamide are dissolved in 500 c.c. of warm water and treated with 500 c.c. of concentrated hydrochloric acid and 200 c.c. of nitric acid (D 1.38). The mixture is evaporated at 60—65° to about one-fifth of its volume, when guanidine nitrate crystallises out in a pure condition. F. M. G. M.

**Production of Putrefaction Bases.** GEORGE BARGER (*Zeitsch. physiol. Chem.*, 1909, 61, 188).—The putrefactive formation of *p*-hydroxyphenylethylamine from tyrosine, which is suggested by Ackermann (this vol., i, 619), has already been proved by Barger and Walpole (this vol., ii, 416). The non-putrefactive formation of putrescine and cadaverine in ergot, observed by Rieländer, is similar to the occurrence of isoamylamine and *p*-hydroxyphenylethylamine in the

same fungus, observed by Barger and Dale (this vol., ii, 689). It is suggested that putrine,  $C_{11}H_{26}O_3N_2$  (Ackermann, Abstr., 1908, i, 10), is derived from Fischer and Abderhalden's diaminotrihydroxydodecanoic acid,  $C_{12}H_{26}O_5N_2$ , by a similar loss of carbon dioxide. G. B.

**Reduction of Amino-acids to Amino-aldehydes.** CARL NEUBERG and E. KANSKY (*Biochem. Zeitsch.*, 1909, 20, 450—462. Compare Neuberg, Abstr., 1908, i, 322; Fischer, *ibid.*, i, 323).—The hydrochlorides of the esters of the amino-acids were reduced in acid solution with sodium amalgam, and the amino-aldehydes isolated as phenyl-osazones and *p*-nitrophenylosazones; some were oxidised with mercuric chloride to pyrazines. The following new substances were prepared: benzoyl derivatives of aminoacetaldehyde and  $\alpha$ -aminopropionaldehyde, syrups, not analysed; *polymeric aminoacetaldehyde*, formed by sodium hydroxide,  $(NH_2 \cdot CH_2 \cdot CHO)_x$ ; *pyrazine aurichloride*,  $C_4H_4N_2 \cdot AuCl_3$ , m. p.  $202^\circ$ ; *p*-nitrophenylosazone of  $\alpha$ -aminopropionaldehyde,

$C_{15}H_{14}O_4N_6$   
(from alanine), m. p.  $277^\circ$ ; 2:5-dimethylpyrazine aurichloride,

$C_6H_8N_2 \cdot AuCl_3$ ,  
m. p.  $153^\circ$ ; *p*-nitrophenylosazone of  $\alpha$ -aminoisovaleraldehyde,

$C_{18}H_{20}O_4N_6$ ,  
m. p.  $256$ — $257^\circ$ . The reduction of isoserine ester probably yielded aminolactaldehyde, but no derivatives of this could be isolated. After treatment with nitrous acid, glyceraldehyde could, however, be isolated as the *p*-nitrophenylosazone. G. B.

**The Next Homologues of Sarcosine and Creatine.** EMIL GANSSER (*Zeitsch. physiol. Chem.*, 1909, 61, 16—68).—In order to facilitate the detection and isolation of the homologues of sarcosine and creatine, which may possibly be present among the products of the hydrolysis of proteins, the preparation and properties of these substances have been investigated.

$\alpha$ -Methylaminopropionic acid crystallises with  $\frac{1}{2}H_2O$  in slender, monoclinic prisms, sinters at  $280^\circ$ , and partly sublimes above  $292^\circ$  (compare Lindenberg, this Journ., 1876, i, 700); the *sulphate* is a hygroscopic, crystalline substance, m. p.  $130$ — $135^\circ$ ; the *hydrochloride*,  $C_4H_9O_2N \cdot HCl$ , forms crystalline nodules; the *platinichloride* ( $2H_2O$ ) crystallises in yellow prisms, m. p.  $202^\circ$  (decomp.); the *copper salt* crystallises with  $2H_2O$ ; the *ethyl ester*,  $C_6H_{13}O_2N$ , is a colourless oil, b. p.  $42$ — $43^\circ/7$  mm.,  $D_4^{20}$  0.9502.  $\alpha$ -Methylaminopropionmethylamide,  $NHMe \cdot CHMe \cdot CO \cdot NHMe$ , obtained by the action of methylamine on ethyl  $\alpha$ -bromopropionate, is a hygroscopic, crystalline mass, which solidifies at  $43.2^\circ$ , b. p.  $110^\circ/8$  mm.; the *platinichloride*, orange-yellow crystals, m. p.  $201^\circ$  (decomp.), and *aurichloride*, lemon-yellow prisms, m. p.  $159$ — $165^\circ$ , were analysed. Contrary to Lindenberg's statement (*loc. cit.*), the action of cyanamide on  $\alpha$ -methylaminopropionic acid in ammoniacal solution leads to the formation of  $\alpha$ -methylguanino-propionic acid lactum (2-imino-5-keto-3:4-dimethyltetrahydroglyoxaline),

$$\begin{array}{c} CO-NH \\ | \\ CHMe \cdot NMe \end{array} > C:NH, \text{ which forms colourless crystals, sinters at about } 270^\circ, \text{ m. p. } 280^\circ \text{ (decomp.)}; \text{ the crystalline hydrochloride, } C_6H_9ON_3 \cdot HCl,$$

has m. p.  $207^{\circ}$ ; the *sulphate*,  $(C_5H_9ON_3)_2 \cdot H_2SO_4$ , forms tufts of light downy needles, m. p.  $232^{\circ}$  (decomp.); the *platinichloride*  $(1H_2O)$  crystallises in small, orange-red, prismatic plates, m. p.  $182-183^{\circ}$  (decomp.).

$\beta$ -Methylaminopropionic acid,  $NHMe \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , prepared by the action of a 33% solution of methylamine on  $\beta$ -iodopropionic acid at  $120^{\circ}$  under pressure, crystallises with  $1H_2O$  in colourless plates, sinters at  $72^{\circ}$ , m. p.  $99-100^{\circ}$ ; the *sulphate*, prismatic needles, m. p.  $130^{\circ}$ , *hydrochloride*, colourless, prismatic needles, m. p.  $105^{\circ}$ , and *platinichloride*, orange-yellow crystals, m. p.  $196^{\circ}$  (decomp.), were analysed; the *copper salt*,  $(C_4H_8O_2N)_2Cu \cdot 6H_2O$ , crystallises in dark blue prisms; the *ethyl ester*,  $C_6H_{13}O_2N$ , is a colourless oil, b. p.  $58^{\circ}/8$  mm.,  $D^{20}_4$  0.9669. The acid interacts with cyanamide, yielding  $\beta$ -methylguaninopropionic acid,  $NH:C(NH_2) \cdot NMe \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , which crystallises with  $1H_2O$  in colourless, compact prisms, m. p.  $201-202^{\circ}$  (decomp.); the *sulphate*, tufts of needles decomposing at  $145^{\circ}$ , *hydrochloride*, colourless flakes, m. p.  $160^{\circ}$ , and *platinichloride*, small, quadratic prisms, m. p.  $195^{\circ}$  (decomp.), were analysed. The corresponding *lactam* could not be isolated, but was obtained in the form of salts; the *hydrochloride*,  $C_5H_9ON_3 \cdot HCl$ , has m. p.  $228^{\circ}$ ; the *platinichloride*,  $(C_5H_9ON_3)_2 \cdot H_2PtCl_6 \cdot 2H_2O$ , forms long, orange, prismatic needles, m. p.  $203^{\circ}$  (decomp.); the *salt*,  $(C_5H_9ON_3 \cdot HCl)_2 \cdot ZnCl_2$ , crystallises in white needles, m. p.  $199-200^{\circ}$ .

$\alpha$ -Methylaminobutyric acid crystallises with  $1H_2O$  in tufts of colourless prisms, and commences to sublime at  $280^{\circ}$  (compare Duvillier, Abstr., 1881, 87); the *mercury salt*,  $(C_5H_{10}O_2N)_2Hg$ , forms crusts of colourless crystals and does not melt below  $260^{\circ}$ ; the *sulphate*,  $(C_5H_{11}O_2N)_2 \cdot H_2SO_4$ ,

crystallises in slender needles, m. p.  $199-200^{\circ}$ ; the *platinichloride*  $(4H_2O)$  crystallises in long, orange-yellow prisms, sinters at  $65-70^{\circ}$ , m. p.  $72^{\circ}$ ; the *anhydrous salt* sinters at  $141^{\circ}$ , m. p.  $150^{\circ}$ , and decomposes at  $210^{\circ}$ ; the *ethyl ester*,  $C_7H_{15}O_2N$ , is a liquid, b. p.  $51-52^{\circ}/8$  mm.,  $D^{20}_4$  0.9348. The *platinichloride* of  $\alpha$ -methylguaninobutyric acid *lactam* (compare Duvillier, Abstr., 1883, 220),

$(C_6H_{11}ON_3)_2 \cdot H_2PtCl_6 \cdot 2H_2O$ , forms dark orange-yellow crystals, m. p.  $186-187^{\circ}$  (decomp.).

$\gamma$ -Methylaminobutyric acid may be prepared by the action of anhydrous methylamine on ethyl  $\gamma$ -chlorobutyrate (compare Tafel and Wassmuth, Abstr., 1907, i, 719); the *hydrochloride* forms thin plates, m. p.  $125^{\circ}$ ; the *platinichloride*  $(2H_2O)$  forms orange-red prisms, m. p.  $85-90^{\circ}$ ; the *anhydrous salt* softens at  $150^{\circ}$ , sinters at  $157^{\circ}$ , m. p.  $160^{\circ}$ , and decomposes at  $202^{\circ}$ ; the *sulphate*,  $(C_5H_{11}O_2N)_2 \cdot H_2SO_4 \cdot 2H_2O$ , crystallises in colourless plates, and passes at  $110^{\circ}$  after several hours into the *hydrogen sulphate*,  $C_5H_{11}O_2N \cdot H_2SO_4$ , a viscid, hygroscopic mass. Attempts to isolate the ethyl ester were unsuccessful, since it readily dissociates into ethyl alcohol and 1-methylpyrrolidone (compare Tafel and Wassmuth, loc. cit.); the *platinichloride* of the latter substance,  $(C_5H_9ON)_2 \cdot H_2PtCl_6 \cdot 2H_2O$ , is a pale yellow, crystalline substance.

$\gamma$ -Methylguaninobutyric acid,  $NH:C(NH_2) \cdot NMe \cdot [CH_2]_3 \cdot CO_2H$ , prepared by the action of cyanamide on  $\gamma$ -methylaminobutyric acid,

crystallises in crusts of small, colourless prisms, m. p.  $307^{\circ}$ ; the crystalline *hydrochloride*, m. p.  $117-126^{\circ}$ , *sulphate*, colourless prisms, m. p.  $245-246^{\circ}$  (decomp.), *nitrate*, colourless crystals, m. p.  $133^{\circ}$ , and *platinichloride*, reddish-brown crystals, m. p.  $190-191^{\circ}$ , were analysed. All attempts to prepare the corresponding lactam were unsuccessful. W. H. G.

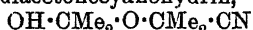
**Preparation of Alkyleneiminosulphonates.** CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 209502).—The interaction of aldehydes and aminosulphonic acids furnishes compounds having the general formula  $\text{CHR}:\text{N}\cdot\text{SO}_3\text{R}_1$ , where R represents hydrogen or a carbon residue and  $\text{R}_1$  a metal or salt-forming group.

*Sodium methyleneiminosulphonate*,  $\text{CH}_2:\text{N}\cdot\text{SO}_3\text{Na}$ , a crystalline powder, m. p.  $125^{\circ}$ , charring at  $230^{\circ}$ , prepared from sodium aminosulphonate and formaldehyde, is readily soluble in water. *Barium ethylideneiminosulphonate*, prepared by the action of acetaldehyde on barium aminosulphonate, forms crystalline leaflets. *Ammonium methyleneiminosulphonate*,  $\text{CH}_2:\text{N}\cdot\text{SO}_3\cdot\text{NH}_4$ , m. p.  $185^{\circ}$ , is decomposed if heated above  $50^{\circ}$  in aqueous solution. These compounds are of therapeutic value. F. M. G. M.

**Cyanohydrins. II. and III.** A. J. ULTÈE (*Rec. trav. chim.*, 1909, 28, 248—256, 257—260. Compare this vol., i, 293).—The cyanohydrins derived from aldehydes are, in general, very little dissociated at the ordinary temperature.

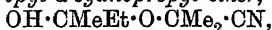
Cyanomethyl alcohol, first prepared by Henry (Abstr., 1890, 739), has  $D_{19}^{19}$  1.1039,  $n_D^{19}$  1.41168. If during its preparation the water is expelled by evaporation on a water-bath at atmospheric pressure, it is very liable to polymerise, becoming dark brown. Cyanomethyl alcohol polymerises very readily in the presence of a trace of alkali.  $\alpha$ -Cyanoethyl alcohol (Gautier, *Ann. Chim. Phys.*, 1869, [iv], 17, 148) has b. p.  $90^{\circ}/17$  mm.,  $D_{14}^{14}$  0.9959,  $n_D^{14}$  1.40644; at  $25^{\circ}$  in the presence of a trace of alkali, acetaldehyde and hydrogen cyanide combine to the extent of 99.55%.  $\alpha$ -Cyano-*n*-propyl alcohol has b. p.  $102-103^{\circ}/23$  mm.,  $D_{15}^{15}$  0.9690,  $n_D^{15}$  1.41745; combination between aldehyde and hydrogen cyanide at  $25^{\circ}$  occurs to the extent of 99.54%.  $\alpha$ -Cyano-*n*-butyl alcohol (Justin, Abstr., 1885, 137) has b. p.  $110.5-111^{\circ}/20.5$  mm.,  $D_{15.5}^{15.5}$  0.9434,  $n_D^{15.5}$  1.42285; combination at equilibrium at  $25^{\circ}$  amounts to 99.69%.  $\alpha$ -Cyanoisobutyl alcohol (Lipp, Abstr., 1881, 84) has b. p.  $106-106.5^{\circ}/22$  mm.,  $D_{16}^{16}$  0.9453,  $n_D^{16}$  1.42215; combination at equilibrium at  $25^{\circ}$  amounts to 99.69%.  $\alpha$ -Cyano-*n*-heptyl alcohol (Gautier, *loc. cit.*) has m. p.  $-10^{\circ}$ , b. p.  $143.5-144^{\circ}/19$  mm.,  $D_{14.5}^{14.5}$  0.9099,  $n_D^{14.5}$  1.43787; the extent of combination at equilibrium at  $25^{\circ}$  is 99.69%. Benzaldehydecyanohydrin cannot be purified by distillation under reduced pressure, but by fractional crystallisation the author has raised the m. p. to  $21.5-22^{\circ}$ ; at  $25^{\circ}$  combination at equilibrium amounts to 95.87%. In the presence of a trace of alkali a small quantity is converted into the acetal,  $\text{CHPh}(\text{O}\cdot\text{CHPh}\cdot\text{CN})_2$ , described by Stollé (Abstr., 1902, i, 468). The cyanohydrin derived from furfuraldehyde could not be obtained, but the *anilino*-derivative,  $\text{C}_4\text{H}_5\text{O}\cdot\text{CH}(\text{NHPh})\cdot\text{CN}$ , was prepared in crystals, m. p.  $74^{\circ}$ , which readily become rose-coloured.

When a mixture of equimolecular quantities of acetone and acetonecyanohydrin [ $\alpha$ -cyanoisopropyl alcohol] are submitted to a current of dry hydrogen chloride and heated in a reflux apparatus for several hours, Urech's diacetonecyanohydrin,



(Abstr., 1873, 59), is formed; it crystallises in needles, m. p.  $162-163^\circ$ .

*a*-Hydroxy- $\alpha$ -methylpropyl  $\alpha$ -cyanopropyl ether,

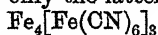


long needles, m. p.  $116-117^\circ$ , is prepared similarly.

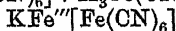
Dicyclohexanonecyanohydrin,  $\text{OH} \cdot \text{C}_6\text{H}_{10} \cdot \text{O} \cdot \text{C}_6\text{H}_{10} \cdot \text{CN}$ , has m. p.  $194^\circ$ .

E. H.

Prussian Blue and Turnbull's Blue. II. ERICH MÜLLER and THEOPHIL STANISCH (*J. pr. Chem.*, 1909, [ii], 80, 153-170. Compare this vol., i, 142).—Solutions of ferric chloride and potassium ferrocyanide, of the same concentrations as before, have been mixed in proportions varying between 9:1 and 1:9, and the resulting precipitates have been examined *in situ* by the methods previously described, the results being checked by an estimation, as sulphate, of the potassium remaining in the solution. The results, which are expressed graphically, lead to the following conclusions. When  $x$ , denoting  $\text{FeCl}_3/\text{K}_4\text{Fe}(\text{CN})_6$ ,  $>1.33$ , the precipitate consists entirely of insoluble Prussian blue,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ , which is unaffected by the excess of ferric chloride. When  $x$  lies between 1.33 and 1.0, the solution does not contain any iron, and the precipitate consists of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  and  $\text{KFe}'''[\text{Fe}(\text{CN})_6]$ , containing only the latter when  $x=1$ . Hence



is changed to  $\text{KFe}'''[\text{Fe}(\text{CN})_6]$  by  $\text{Fe}(\text{CN})_6$  ions. When  $x < 1.0$ , the ratio of the non-ionisable to the ionisable iron in the precipitate is always unity, but that of the ferrous to the ferric iron increases with the amount of potassium ferrocyanide. The precipitate consists of  $\text{KFe}'''[\text{Fe}(\text{CN})_6]$  and  $\text{K}_2\text{Fe}''[\text{Fe}(\text{CN})_6]$ , and the reactions which occur are (i)  $\text{FeCl}_3 + \text{K}_4\text{Fe}(\text{CN})_6 = \text{KFe}'''[\text{Fe}(\text{CN})_6] + 3\text{KCl}$  and (ii)  $\text{FeCl}_3 + 2\text{K}_4\text{Fe}(\text{CN})_6 = \text{K}_2\text{Fe}''[\text{Fe}(\text{CN})_6] + \text{K}_3\text{Fe}(\text{CN})_6 + 3\text{KCl}$ . Hence

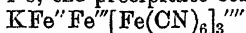


is reduced by  $\text{Fe}(\text{CN})_6$  ions, and the reaction  $\text{KFe}'''[\text{Fe}(\text{CN})_6] + \text{K}_4\text{Fe}(\text{CN})_6 \rightleftharpoons \text{K}_2\text{Fe}''[\text{Fe}(\text{CN})_6] + \text{K}_3\text{Fe}(\text{CN})_6$  must be reversible, since the solution still contains  $\text{Fe}(\text{CN})_6$  ions when  $x=0.5$ . It should be noted that the precipitate does or does not contain potassium according as  $x < \text{or} > 1.33$ , and also that ionisable ferrous iron is present or not in the precipitate according as  $x < \text{or} > 1.0$ .

The results are almost the same when the precipitations are effected in 0.1*N*-hydrochloric acid.

Exactly similar experiments have been performed with solutions of ferrous chloride and potassium ferricyanide. It has been shown previously (*loc. cit.*) that the precipitates are always ferrocyanides. When  $y$ , denoting  $\text{FeCl}_2/\text{K}_3\text{Fe}(\text{CN})_6$ ,  $>1.33$ , the ratio of ferrous to ferric iron in the precipitate is always 1.33, and that of the non-ionisable to the ionisable iron is 0.75. Hence the reaction is:  $3\text{K}_3\text{Fe}(\text{CN})_6 + 4\text{FeCl}_2 = \text{KFe}''\text{Fe}_3'''[\text{Fe}(\text{CN})_6]_3 + 8\text{KCl}$ , and the precipitate of insoluble

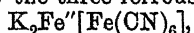
Turnbull's blue is unaffected by the excess of ferrous chloride. When  $y$  lies between 1.33 and 1.0, the precipitate contains



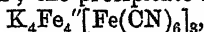
and  $KFe'''[Fe(CN)_6]'''$ , and consists of the latter alone when  $y = 1$ . When  $y < 1$ , the precipitate always consists of  $KFe'''[Fe(CN)_6]'''$ , which is therefore unchanged by an excess of potassium ferricyanide. All Turnbull's blues, the precipitates obtained from ferrous salts and potassium ferricyanide, contain potassium.

The authors' and Hofmann's experiments (this vol., i, 637) are not comparable, since the latter deal with precipitates after atmospheric oxidation. C. S.

**Ferrous Ferrocyanides.** ERICH MÜLLER and W. TREADWELL (*J. pr. Chem.*, 1909, [ii], 80, 170—182. Compare preceding abstract).—The effects of the reactions of aqueous solutions of ferrous chloride and potassium or hydrogen ferrocyanide, of heating potassium ferrocyanide and dilute sulphuric acid, and of heating an aqueous solution of hydrogen ferrocyanide, all in an atmosphere of hydrogen or carbon dioxide, have been examined and the precipitates analysed *in situ* by the methods already described. The results are not conclusive, but it appears probable that only the three ferrous ferrocyanides,



$K_4Fe_4''[Fe(CN)_6]_3$ , and  $Fe_2''[Fe(CN)_6]$ , can exist. The last is formed when an aqueous solution of hydrogen ferrocyanide is heated until hydrogen cyanide ceases to be evolved. The two compounds containing potassium are precipitated from solutions containing potassium, ferrocyanogen, and ferrous ions; the precipitate is mainly



when potassium ferrocyanide reacts with a large excess of ferrous chloride, whilst  $K_2Fe''[Fe(CN)_6]$  is the chief product under the converse conditions or when potassium ferrocyanide is heated with 0.5*N*-sulphuric acid. C. S.

[Stable Soluble Compounds of Organic Substances and Silver Double Salts.] ALBERT BUSCH (D.R.-P. 209345. Compare Abstr., 1907, i, 370).—The compound of hexamethylenetetramine with silver carbonate,  $5C_6H_{12}N_4 \cdot 3Ag_2CO_3 \cdot 15H_2O$ , can be rendered soluble and stable by digestion with albumen, after which hydrogen sulphide, ammonium sulphide, or dilute sodium chloride solutions give no precipitate of silver salts.

Albumen (70 parts) is dissolved in 200 parts of water and heated to 40—50°, the double carbonate (30 parts) is added, and the heating continued at a lower temperature and evaporated, preferably in a vacuum. The product contains 7.5% of silver. F. M. G. M.

**Preparation of 2:6-Dichloro- and 2:3:6-Trichloro-toluene-4-sulphonyl Chlorides.** ANILINFARBEN UND EXTRAKT-FABRIKEN VORM. J. R. GEIGY IN BASEL (D.R.-P. 210856).—*p*-Toluenesulphonyl chloride is treated at 70—75° with sufficient antimony pentachloride to furnish 2—3 atoms of chlorine. When cool, the mass is hydrolysed with alkali to a mixture of the corresponding acids, or the acyl group

can be completely removed and the resulting mixture of 2:6-di- and 2:3:6-tri-chlorotoluenes separated by fractional distillation.

F. M. G. M.

**Sulphonation of Naphthalene. Quantitative Examination.** P. C. J. EUWES (*Rec. trav. chim.*, 1909, 28, 298—338).—When equimolecular quantities of naphthalene and 100% sulphuric acid are heated for eight hours, the product at 80° consists almost wholly of the  $\alpha$ -sulphonic acid. As the temperature employed rises, the proportion of  $\beta$ -acid formed increases, reaching a maximum between 150° and 160°, above which temperature considerable quantities of sulphone and disulphonic acid are produced. The amount of naphthalene remaining unattacked diminishes from 27% at 80° to 6% at 161°.

Experiments in which the duration of heating was varied show that the primary product of sulphonation is the  $\alpha$ -acid, which is gradually transformed into the  $\beta$ -isomeride. Thus after thirty-five minutes at 129° the product contains 79.1% of the  $\alpha$ -acid, whilst after six hours the proportion is reduced to 45.1%. At 143° and 158°, however, conditions of equilibrium are attained, and may be reached either by sulphonating naphthalene or by heating lead naphthalene- $\beta$ -sulphonate with equivalent weights of sulphuric acid and water.

The author accepts the explanation offered by Merz and Weith (*Ber.*, 1870, 3, 195) and by Friedländer and Lucht (*Abstr.*, 1894, i, 138), that the transformation is due to the hydrolysis of the two acids into naphthalene and sulphuric acid, and subsequent resulphonation, the  $\alpha$ -acid being more stable at low, and the  $\beta$ -acid at high, temperatures. This view is supported by the observations that, when either acid is heated in a medium containing water, naphthalene is formed, and that the  $\beta$ -acid is not converted into its isomeride when heated with fuming sulphuric acid at 129°.

At 129° the product of heating the  $\beta$ -sulphonic acid with sulphuric acid has not the same composition as the product of sulphonating naphthalene at this temperature. In explanation of this, the author suggests that at 129° the above hydrolysis is largely replaced by an irreversible intramolecular change of the  $\alpha$ - into the  $\beta$ -acid, the change being effected catalytically by sulphuric acid, but inhibited when the latter contains a certain amount of water or the reaction product.

The presence of water in the sulphuric acid used for sulphonating naphthalene diminishes the amount of hydrocarbon attacked, and largely accelerates the transformation of the  $\alpha$ -acid, equilibrium being reached with 96% sulphuric acid in two hours instead of the six hours required with 100% acid. Addition of sulphur trioxide largely increases the amount of sulphone formed, whilst phosphoric oxide causes the production of much disulphonic acid.

Lead and mercuric sulphates have practically no effect on the reaction. E. H.

**Action of Bromine on  $\beta$ -Methylnaphthalene in the Presence of Aluminium Bromide.** F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1909, [iv], 5, 826—827).—In the presence of aluminium bromide, bromine reacts with  $\beta$ -methylnaphthalene, furnishing penta-

*bromo-β-methylnaphthalene*,  $C_{10}H_7MeBr$ , which forms slender, white needles, m. p. 285—286°. E. H.

**Doubly Linked Carbon Atoms and the Carbon Nitrogen Linking.** HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 314—332).—It is well known that the single linking between the carbon and the nitrogen atoms is frequently easily ruptured when the group C·N is in the neighbourhood of an olefinic linking. The author quotes numerous examples from the literature to illustrate in what circumstances such is the case, and the conclusions are drawn that in the combination C:C·N a loosening of the union between carbon and nitrogen is effected by an olefinic linking, but not by the benzene double linking (centric linking), and also that a similar loosening in the combination C:C·C·N is caused by olefinic or centric linkings, but in the former case only when the olefinic linking is present in a large group, such as cinnamyl, not in a smaller radicle, such as allyl. As typical examples, neurine in aqueous solution readily loses trimethylamine, aniline is a stable substance, cinnamyltrimethylammonium chloride and sodium amalgam yield phenylpropylene and trimethylamine, whilst trimethylallyl-ammonium chloride is unaffected by nascent hydrogen in either acid or alkaline solution. C. S.

**Doubly Linked Carbon Atoms and the Carbon Nitrogen Linking. II. Cinnamylamino-compounds.** HERMANN EMDE and MAX FRANKE (*Arch. Pharm.*, 1909, 247, 333—350. Compare this vol., i, 565 and following abstracts).—Cinnamyl chloride and 10% alcoholic ammonia in eight days at the ordinary temperature yield mono- and di-cinnamylamine, whilst at 100° in three days, according to Posner, the secondary and tertiary bases are the chief products. The authors now find that the number of hydrogen atoms in ammonia replaced by the cinnamyl group increases with the concentration of the ammonia. When cinnamyl chloride, concentrated methyl alcoholic ammonia, and ether are kept for fourteen days, the chief product is a crystalline *chloride*, m. p. 189° (*nitrate*, m. p. 201°; *iodide*, m. p. 176°), which is also obtained by heating cinnamyl chloride and tricinnamylamine at 100° for thirty minutes; although the analytical data point to the composition  $C_{73}H_{73}N_3Cl_2$ , the authors provisionally regard the substance as tetracinnamylammonium chloride, since it is converted by sodium amalgam into tricinnamylamine and phenylpropylene.

The remainder of the paper is a description of the behaviour of cinnamyl chloride with different amines. With cold 33% alcoholic dimethylamine it yields dimethylamine hydrochloride, *cinnamyl dimethylamine hydrochloride*, m. p. 188° [*platnichloride*,  $(C_{22}H_{30}N_2)_2PtCl_6$ , m. p. 140°], and *dicinnamyl dimethylammonium chloride* [*platnichloride*,  $(C_{20}H_{24}N)_2PtCl_6$ , m. p. 192°; *cadmichloride*,  $(C_{20}H_{24}N)_2CdCl_4$ , m. p. 161°]. With ethereal ethylamine at 0°, it yields ethylamine hydrochloride and *tricinnamylethylammonium chloride*, m. p. 188° [*platnichloride*,  $(C_{29}H_{32}N)_2PtCl_6$ , m. p. 184°]. With triethylamine in five days it yields *cinnamyl triethylammonium chloride* [*platnichloride*,  $(C_{15}H_{24}N)_2PtCl_6$ , m. p. 180°; *aurichloride*,  $(C_{15}H_{24}N)AuCl_4$ , m. p. 107°]. With ethereal

propylamine it yields *dicinnamylpropylamine hydrochloride*, m. p. 167° [*platinichloride*,  $(C_{21}H_{21}N)_2PtCl_6$ , m. p. 122°]. With tripropylamine it yields *cinnamyltripropylammonium chloride* [*platinichloride*,  $(C_{18}H_{30}N)_2PtCl_6$ , m. p. 197°; *aurichloride*, m. p. 96°]. With ethereal aniline it yields *dicinnamylaniline*, m. p. 88° [*platinichloride*,  $(C_{24}H_{23}N)_2PtCl_6$ , m. p. 173° decomp.]. With methylaniline, it yields a red oil, which appears to be *phenyldicinnamylmethylammonium chloride* [unstable *platinichloride*,  $(C_{25}H_{26}N)_2PtCl_6$ , m. p. 117° decomp.]. With dimethylaniline in fourteen days, it yields *phenylcinnamyltrimethylammonium chloride* [*platinichloride*,  $(C_{17}H_{20}N)_2PtCl_6$ , m. p. 177° decomp.; *cadmichloride*,  $(C_{17}H_{20}N)_2CdCl_4$ , m. p. 141°]. With quinoline in three days it yields *cinnamylquinolinium chloride* [*platinichloride*,  $(C_{18}H_{16}N)_2PtCl_6$ , m. p. 202°; *aurichloride*, m. p. 228°]. C. S.

**Doubly Linked Carbon Atoms and the Carbon Nitrogen Linking. III. Methylated Benzylamines.** HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 351—368).—The reaction between methyl iodide, benzylamine, and methyl alcohol is not a convenient method for the preparation of methylated benzylamines, since the crystalline product is a difficultly separable mixture of iodides of constant m. p., 133.5°. Dibenzylamine, methyl alcohol, and methyl iodide (1 mol.) react to form dibenzylamine hydriodide, *dibenzylidimethylammonium iodide*, m. p. 191° (*platinichloride*, m. p. 208° decomp.), and a *periodide* of dibenzylmethylamine,  $C_{35}H_{54}N_3I_4$ , m. p. 155°.

Methylated benzylamines are conveniently obtained by the interaction of benzyl chloride and the methylamines. The action of benzyl chloride on trimethylamine has been examined by Collie and Schryver (*Trans.*, 1890, 57, 778), and on dimethylamine by Jackson and Wing (*Abstr.*, 1887, 721). Benzyl chloride and 33% alcoholic methylamine (>2 mol.) react at 0° to form methylamine hydrochloride, benzylmethylamine, and *dibenzylmethylamine*, b. p. 304—305° (corr.), which forms a *platinichloride*, m. p. 192° (decomp.), and two *aurichlorides*,  $C_{15}H_{17}N, HAuCl_4$ , m. p. 135°, and  $C_{30}H_{38}N_2Cl_5Au$ , m. p. 134—136°, the former being obtained by adding a concentrated solution of the hydrochloride to an excess of 10% gold chloride, and the latter by adding 10% gold chloride to a dilute solution of the hydrochloride.

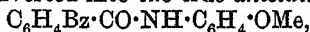
C. S.

**Doubly Linked Carbon Atoms and the Carbon-Nitrogen Linking. IV. Behaviour of Quaternary Ammonium Compounds towards Nascent Hydrogen.** HERMANN EMDE (*Arch. Pharm.*, 1909, 247, 369—391. Compare this vol., i, 565 and preceding abstracts).—The comparative stability of the systems C:C·N and C:C·C·N has been examined during the continuation of previous work. In addition to the results previously recorded, the author finds that aqueous or dilute alcoholic solutions of cinnamyltrimethylammonium chloride, cinnamyltripropylammonium chloride, dicinnamyltrimethylammonium chloride, phenyldicinnamylmethylammonium chloride and tricinnamylethylammonium chloride suffer reductive

fission by treatment with 5% sodium amalgam, yielding phenylpropylene and the tertiary amine, whilst benzyltrimethylammonium chloride in a similar manner yields trimethylamine and toluene. Cinnamylpyridinium chloride, cinnamylquinolinium chloride, trimethylallylammonium iodide, and phenyltrimethylammonium iodide do not behave in a similar way by treatment with sodium amalgam. The preceding reductive fissions are not effected by nascent hydrogen in acid solution.

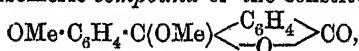
C. S.

**Anilides and Anisidides of Aromatic Ketonic and Aldehydic Acids.** HANS MEYER and RICHARD TURNAU (*Monatsh.*, 1909, 30, 481—496. Compare Abstr., 1908, i, 25).—Equal weights of *p*-anisidine and *o*-benzoylbenzoic acid, when heated together over an oil-bath and subsequently over a water-bath, yielded a *ψ*-anisidide,  $C_{21}H_{17}O_3N$ , which crystallises in colourless needles, m. p.  $198^\circ$ ; this substance can be titrated directly with 10% potassium hydroxide, and when treated with phenylhydrazine its anisidine residue is replaced by the phenylhydrazine with the formation of the phenylhydrazone of *o*-benzoylbenzoic acid, m. p.  $168^\circ$  (compare Abstr., 1885, 797, 1905, i, 133). The *ψ*-anisidide is converted into the true *anisidide*,



by gently boiling for twenty minutes with twenty times its weight of acetic anhydride; this substance crystallises in colourless needles, m. p.  $204^\circ$ ; it is neutral to potassium hydroxide, and no longer reacts with phenylhydrazine.

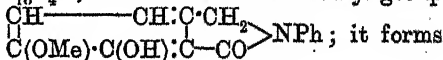
A 70% yield of *p*-methoxybenzoylbenzoic acid was obtained by heating a solution of phthalic anhydride and anisole in nitrobenzene with aluminium chloride; its m. p.,  $148^\circ$ , is rather higher than that quoted by Nourisson (Abstr., 1886, 1029). It yields two isomeric methyl derivatives; the *methyl ester*,  $CO_2Me \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot OMe$ , m. p.  $63^\circ$ , is obtained by the action of methyl sulphate on *p*-hydroxybenzoylbenzoic acid; the isomeric *compound* of the constitution



obtained by the action of thionyl chloride on *p*-methoxybenzoylbenzoic acid, has m. p.  $84^\circ$ . The study of the reaction between anisidine and anisoylbenzoic acid was commenced, but has not yet been brought to a satisfactory conclusion.

The *ψ*-anilide of opianic acid described by Liebermann is converted into the true *anilide*,  $C_{16}H_{15}O_4N$ , by boiling with excess of acetic anhydride; it crystallises in leaflets, m. p.  $179^\circ$ ; when heated with phenylhydrazine it is converted into the *hydrazone* of opianic acid,  $C_{22}H_{21}O_3N_3$ , pale yellow needles, m. p.  $204^\circ$ . The *ψ*-anilide of opianic acid is reduced by zinc and acetic acid to a compound,  $C_{16}H_{15}O_3N$ , which forms slender needles, m. p.  $141^\circ$ .

Meconine and aniline heated together in presence of aniline hydrochloride do not yield the *ψ*-anilide of opianic acid, but give instead *methylnormeconineanilide*,  $C_{16}H_{16}O_4N$ , which contains one methyl group less, and has the constitution



colourless, glistening leaflets, m. p. 164°; its *acetyl* derivative forms slender needles, m. p. 161°.

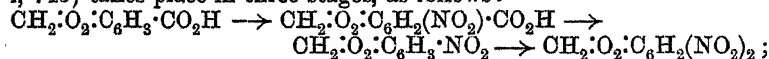
The anilide of meconine, when heated with aniline and aniline hydrochloride, also yields methylnormeconine anilide; the latter compound does not react with methyl sulphate. P. H.

**Preparation of Nitro-1:8-naphthasultamsulphonic Acid and 2:4-Dinitro-1:8-naphthasultam.** FAPBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 210222).—When 1:8-naphthasultam-2:4-disulphonic acid is treated at 75–80° with nitric acid (D 1·2), either one or both the sulphonic groups are replaced by a nitro-group. In the presence of 50% sulphuric acid, the mono- or di-nitro-compound is formed, according to the amount of nitric acid employed; whilst in the absence of sulphuric acid, but with a greatly increased quantity of nitric acid, the dinitro-compound alone is obtained.

*Sodium nitro-1:8-naphthasultamsulphonate* is a crystalline, yellow powder, which dyes wool a yellow colour. 2:4-Dinitro-1:8-naphthasultam, m. p. 262° (with decomp.), is a deep yellow powder, which forms a salt when dissolved in sodium carbonate or hydroxide; it also dissolves readily in hot alcohol, but only sparingly in the cold solvent or in water. F. M. G. M.

**4:5-Dinitro-1:2-catechol Methylene Ether.** [4:5-Dinitro-1:2-methylenedioxybenzene.] EFISIO MAMELI (*Gazzetta*, 1909, 39, ii, 172–186).—The author describes the methods by which he has established the constitution of dinitromethylenedioxybenzene (compare Abstr., 1906, i, 743), which is of especial interest as it forms the final product of the energetic nitration of compounds containing the methylenedioxybenzene grouping, even when the positions occupied by the nitro-groups are previously filled by carboxyl groups, or by lateral chains. The formation of this dinitro-compound hence serves as a test for such grouping, which occurs in many natural products.

The formation of dinitromethylenedioxybenzene from piperonylic acid (compare Jobst and Hesse, Abstr., 1878, 733; Mameli, 1904, i, 743) takes place in three stages, as follows:



each of these stages has been realised by the author.

That one of the nitro-groups in dinitromethylenedioxybenzene occupies the 4-position with respect to the methylenedioxy-group is shown by the formation of this compound from nitropiperonylic acid and nitromethylenedioxybenzene. That the second nitro-group is in the *o*-position to the first is shown by the formation from an alcoholic solution of dinitromethylenedioxybenzene, by the action of gaseous ammonia, of a nitroaminomethylenedioxybenzene, which, by reduction with zinc and acetic acid and condensation of the reduction product with phenanthraquinone, yields the corresponding phenazine. That this second nitro-group occupies the 5- and not the 3-position is shown by diazotising the nitroaminomethylenedioxybenzene and replacing the diazo-group by cyanogen, the compound thus obtained being identical with that obtained by dehydrating the oxime of 2-nitro-4:5-

methylenedioxybenzaldehyde. The two nitro-groups in dinitromethylenedioxybenzene are hence in the 4- and 5-positions with respect to the methylenedioxy-group.

4-Nitro-5-aminomethylenedioxybenzene,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2(\text{NO}_2)\cdot\text{NH}_2$ , crystallises in shining, red laminae, or tufts of acicular crystals, m. p. 199°. The phenazine obtained from the corresponding diamino-compound,  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2:\text{N}_2(\text{C}_{14}\text{H}_8)$ , forms a dark yellow, crystalline powder, m. p. 305°, which sublimes in slender, golden-yellow needles, and dissolves in sulphuric acid, giving a reddish-violet coloration.

T. H. P.

**Preparation of Phthalimidocatechol Ethers.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 209962).—*Phthalimidoacetylveratrole*, m. p. 202°, white powder insoluble in alcohol, is obtained by heating together on the water-bath equal weights of veratrole, phthalylglycyl chloride, and aluminium chloride. The mixture is treated successively with water and dilute hydrochloric acid, the unchanged veratrole removed in a current of steam, and the residue purified by extraction with alcohol.

*α-Phthalimidopropionyl chloride*, white crystals, m. p. 71°, is produced by treating dry *α*-phthalimidopropionic acid, m. p. 160° (phthalyl-*α*-alanin), with phosphorus pentachloride on the water-bath until a solution is obtained; the phosphoryl chloride is distilled off in a vacuum, and the product crystallised from petroleum. The foregoing acid chloride is fused on the water-bath with an equal weight of veratrole, and, after cooling, the same quantity of aluminium chloride introduced.

*α-Phthalimidopropionylveratrole*, white powder, m. p. 212°, is isolated in a manner similar to that employed for its lower homologue.

*β-Phthalimidopropionylveratrole*, colourless needles, m. p. 175°, is prepared in the same way from *β*-phthalimidopropionyl chloride.

F. M. G. M.

**Homocatechol and its Methyl Ethers.** O. DE VRIES (*Rec. trav. chim.*, 1909, 28, 276—297).—Homocatechol, prepared from creosol by Stoermer's method (Abstr., 1908, i, 190), has m. p. 65° (Béhal and Desvignes give 51°, Abstr., 1892, 1312; Cousin gives 49—50°, Abstr., 1899, i, 346),  $D_{25}^{23.6}$  1.1567,  $D_4^{23.6}$  1.1287,  $n_D^{23.6}$  1.5373,  $n_D^{23.6}$  1.5425,  $n_F^{23.6}$  1.5560,  $n_G^{23.6}$  1.5678.

By cooling in liquid air, creosol has been solidified in large, colourless prisms, m. p. 5.5° (thermometer in liquid). At the ordinary temperature it is a colourless oil,  $D_{25}^{25}$  1.0951 (Perkin, Trans., 1896, 69, 1185, gives 1.0886),  $D_{38.6}^{25}$  1.0867,  $D_4^{25}$  1.0919,  $D_4^{38.6}$  1.0789,  $n_C^{25}$  1.5303,  $n_D^{25}$  1.5353,  $n_F^{25}$  1.5483,  $n_G^{25}$  1.5596,  $n_C^{38.6}$  1.5237,  $n_D^{38.6}$  1.5288,  $n_F^{38.6}$  1.5418,  $n_G^{38.6}$  1.5530.

Creosol picrate forms orange-yellow needles, m. p. 112° (corr.) (Goedike, Abstr., 1894, i, 119, and Bamberger and Vischner, Abstr., 1901, i, 220, give m. p. 96°).

For *m*-nitro-*p*-cresol, an intermediate compound in the synthesis of isocresol by Brasch and Freyss' method (Abstr., 1891, 1231), the author finds m. p. 32.5° (corr.), b. p. 114.5°/7.5 mm.,

125°/22 mm., whilst Hofmann and Miller (Abstr., 1881, 592) gave m. p. 33°, Noelting and Wild (Abstr., 1885, 973) 33·5°, Brasch and Freyss 36·5° (non-corr.) and Upson (Abstr., 1904, i, 734) 34°. The author's specimen was purified through the sodium salt, which was recrystallised from alcohol. The substance has  $D_{25}^{38\cdot6}$  1·2489,  $D_4^{38\cdot6}$  1·2399,  $n_D^{25}$  1·5720,  $n_D^{38\cdot6}$  1·5828,  $n_F^{38\cdot6}$  1·5657,  $n_D^{38\cdot6}$  1·5763.

The methyl ether, hitherto only obtained as an oil, forms beautiful large crystals, m. p. 8·5° (corr. thermometer in substance), b. p. 159°/15 mm,  $D_{25}^{38}$  1·2059,  $D_4^{38}$  1·2025,  $n_D^{25}$  1·5458,  $n_D^{38}$  1·5536,  $n_F^{38}$  1·5737. The observed m. p. of isocresol is 35·5° (corr.), whilst Perkin gave 37—39° (*loc. cit.*). isoCresol has  $D_{25}^{38\cdot6}$  1·0820,  $D_4^{38\cdot6}$  1·0742,  $n_D^{38\cdot6}$  1·5219,  $n_D^{38\cdot6}$  1·5269,  $n_F^{38\cdot6}$  1·5396,  $n_G^{38\cdot6}$  1·5504. isoCresol picrate forms crystals, m. p. 87·5°.

Homoveratrole, hitherto obtained only as an oil, forms large, colourless prisms, m. p. 21° (corr. thermometer in substance),  $D_{25}^{38}$  1·0540, (Perkin gave 1·0525),  $D_4^{38}$  1·0509,  $n_D^{38}$  1·5209,  $n_D^{38}$  1·5257,  $n_F^{38}$  1·5383,  $n_G^{38}$  1·5493.

Comparison of the physical constants obtained for homocatechol, cresol, isocresol, and homoveratrole shows that, on the whole, they are in accordance with the general rules. As found generally by Brühl (Trans., 1907, 91, 115), there is a small exaltation of the observed over the calculated refractive indices and dispersive powers. The exaltations of the dispersive powers for the hydroxy- and methoxy-groups are approximately the same as those found in other phenols. E. H.

**Tannin Methyl Ether.** JOSEF HERZIG and V. RENNER (*Monatsh.*, 1909, 30, 543—554. Compare Herzig and Tscherne, Abstr., 1905, i, 354).—Since tannin methyl ether is an amorphous substance, its degree of purity is determined better by a methoxyl estimation than by ultimate analysis. Tannin methyl ether is practically unaffected by further treatment with diazomethane, and also by a mixture of boiling glacial acetic acid, zinc, sodium acetate, and acetic anhydride. Its decomposition by 10% potassium hydroxide is slow, and the undissolved portion, after five to six hours' treatment, possesses the same properties as the original substance. It appears very probable, therefore, that tannin methyl ether either is an individual substance or consists of substances which have not only nearly the same composition, but also contain the same number of substituted hydroxyl groups. The authors retain this opinion despite the fact that the rotation of tannin methyl ether varies greatly according to the treatment it receives.

The decomposition of tannin methyl ether by potassium hydroxide with the production of gallic acid di- and tri- methyl ethers has been examined by Herzig and Tscherne (*loc. cit.*). The authors have repeated the experiments, using 10% potassium hydroxide, and confirm the previous results. They show also that the ethers are stable to the potassium hydroxide, and that no other decomposition product can be detected.

From the two constitutions proposed by Nierenstein for the two constituents which he claims to be present in commercial tannin, it appears probable that tannin methyl ether is a pentamethoxy-derivative of either or of both constituents. C. S.

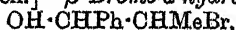
**Cholesterol.** IV. J. MAUTHNER (*Monatsh.*, 1909, 30, 635—647. Compare Abstr., 1907, i, 921).—Windaus's claim that the constitution of  $\psi$ -cholestene differs from that of cholestene only in a shifting of the olefinic linking from the ultimate to the penultimate pair of carbon atoms in the side-chain is untenable, since the two unsaturated hydrocarbons yield, by the addition of hydrogen, isomeric and not identical saturated hydrocarbons, cholestane and  $\psi$ -cholestane. The existence of these two isomeric saturated hydrocarbons, one of which is obtained directly, and the other indirectly, from cholestene, does not harmonise with the theory of a terminal methylene group in cholestene, and gives rise to the question, which still awaits an answer, whether cholestene really has a constitution similar to that of cholesterol.

**Cholestene**,  $C_{27}H_{46}$ , m. p.  $80^\circ$ , obtained by passing hydrogen for fifty to seventy hours through an ethereal solution of cholestene in the presence of platinum-black, crystallises in leaflets and has  $[\alpha]_D + 24.42^\circ$  in chloroform.  **$\psi$ -Cholestene**,  $C_{27}H_{46}$ , m. p.  $69-70^\circ$ , obtained in a similar manner from  $\psi$ -cholestene, crystallises in needles, and has  $[\alpha]_D + 25.45^\circ$  in chloroform. A mixture of equal weights of the two hydrocarbons has m. p.  $50-51^\circ$ . **Chlorocholestene**,  $C_{27}H_{45}Cl$ , m. p.  $115-116^\circ$ , obtained in a similar way from cholesteryl chloride, has  $[\alpha]_D + 29.49^\circ$  in chloroform and  $24.22^\circ$  in benzene. The halogen is firmly retained, and is practically unattacked by fourteen hours' boiling with zinc dust and zinc acetate in glacial acetic acid or by boiling solutions of sodium methoxide and sodium amyl oxide. Chlorocholestene is reduced, however, to cholestane by sodium and boiling amyl alcohol.

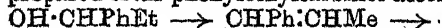
**neoCholestene**,  $C_{27}H_{44}$ , m. p.  $69^\circ$ ,  $[\alpha]_D + 64.07$ , is an unsaturated hydrocarbon obtained by boiling chlorocholestene with quinoline for one to two hours. It forms a *dibromide*,  $C_{27}H_{44}Br_2$ , m. p.  $125^\circ$ ,  $[\alpha]_D^{25} + 75.27^\circ$ , and is reduced in ethereal solution by hydrogen and platinum-black to cholestane, thus proving that *neocholestene* and cholestene differ only in the position of the double linking. C. S.

**Saturated  $\alpha$ -Hydroxy- $\beta$ -alkyloxy-derivatives of Aromatic Olefines with Propenyl Chains.** EFISIO MAMELI (*Gazzetta*, 1909, 39, ii, 154—165).—The author has studied the action of alkali alkyl oxides on  $\beta$ -bromo- $\alpha$ -hydroxydihydro-derivatives of the following aromatic compounds containing the propenyl group, in order to ascertain whether the corresponding  $\alpha$ -hydroxy- $\beta$ -alkyloxy-derivatives are obtained: propenylbenzene, anethole, *isosafole*, asarone, and *isoapiole*. The results show the possibility of the formation of certain  $\alpha$ -hydroxy- $\beta$ -alkyloxy-derivatives of the type  $OH \cdot CHR \cdot CHMe \cdot OMe$ , substitution of the bromine in the  $\beta$ -position by the alkyloxy-group failing only when the latter is met by steric hindrance within the molecule; this is the case with the  $\beta$ -bromo- $\alpha$ -hydroxy-derivatives of bromo*isosafole* and bromo*isoapiole*.

[With EDOARDO BROCCA].— $\beta$ -Bromo- $\alpha$ -hydroxy- $\alpha$ -phenylpropane,



prepared from phenylethylcarbinol according to the scheme:



is a greenish-yellow, oily liquid, b. p. 126—129°/45 mm., with an extremely irritating odour.

*a*-Hydroxy- $\beta$ -methoxy- $\alpha$ -phenylpropane,  $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{OMe}$ , prepared by the action of sodium methoxide on  $\beta$ -bromo- $\alpha$ -hydroxy- $\alpha$ -phenylpropane, is a colourless oil, b. p. 145—147°/70—80 mm.

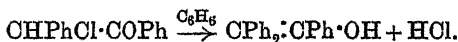
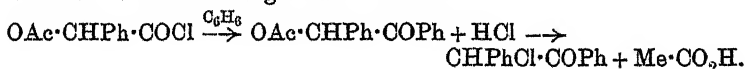
[With CESARE BIGNAMI.]—*a*-Hydroxy- $\beta$ -methoxydihydroanethole,  
 $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{OMe}$ ,

prepared by the action of sodium methoxide on the hydroxy-bromide,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CHMeBr}$  (compare Höring, *Abstr.*, 1906, i, 951), is an oily liquid, b. p. 171—175°/65—70 mm.

[With RAIMONDO BONU.]— $\beta$ -Bromo- $\alpha$ -hydroxydihydroisosafole, in ethereal solution at 0°, absorbs hydrogen chloride, forming a mixture of chloro- and bromo-derivatives from which no definite product could be separated. In ethereal solution, it also combines slowly with sodium, but yields no definite compound. It reacts vigorously with concentrated nitric acid, giving a resinous mixture of nitro-derivatives. When treated with sodium methoxide, it yields *a*-hydroxy- $\beta$ -methoxydihydroisosafole,  $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{OMe}$ , as a colourless oil, b. p. 182—185°/10—20 mm.,  $D^{20}_D$  1.19; the corresponding *acetyl* derivative,  $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{OAc})\cdot\text{CHMe}\cdot\text{OMe}$ , is a colourless oil, b. p. 200—205°/10—20 mm. T. H. P.

**Action of Benzene and Aluminium Chloride on the Chlorides of Acetylated Hydroxy-acids.** RICHARD ANSCHÜTZ and PAUL FÖRSTER (*Annalen*, 1909, 368, 89—94. Compare Anschütz, *Abstr.*, 1906, i, 516).—It was thought possible that benzoylcarbonyl acetate would be obtained by acting on a solution of acetylglucosyl chloride (acetoxyacetyl chloride) in benzene with aluminium chloride, but although this compound is probably formed, it must be decomposed at once by the hydrogen chloride, yielding benzoylcarbinol and acetyl chloride, which latter substance reacts with benzene under the influence of the aluminium chloride, forming acetophenone.

Acetylmandelyl chloride, when similarly treated, does not yield benzoin acetate, but triphenylvinyl alcohol, which probably owes its formation to the following series of reactions:



This explanation receives support from the fact that triphenylvinyl alcohol is readily obtained by the action of aluminium chloride on a solution of desyl chloride in benzene. W. H. G.

**Benzoyl Iodide and its Relation towards Simple Ethers.** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 651—659).—The interaction of benzoyl chloride and the compound of magnesium iodide with ether yields 45% of the quantity of benzoyl iodide calculated from the equation:  $\text{MgI}_2 + 2\text{Ph}\cdot\text{COCl} = \text{MgCl}_2 + 2\text{Ph}\cdot\text{COI}$ . The amount of ethyl benzoate formed at the same time is 26.6% of the quantity calculated on the assumption that the reaction proceeds according to Blaise's scheme (*Abstr.*, 1905, i, 111). Benzoyl iodide (compare Liebig and Wöhler, *Annalen*, 1832, 266) forms acicular

crystals, m. p.  $+3^{\circ}$ . At the ordinary temperature it is slowly but completely decomposed by water, or by an alkali carbonate or hydroxide. Concentrated ammonia solution acts on it very readily, yielding ammonium benzoate and benzamide. In absence of a magnesium salt it reacts readily with ethers according to the equation:  $\text{Ph}\cdot\text{COI} + \text{R}\cdot\text{O}\cdot\text{R} = \text{RI} + \text{Ph}\cdot\text{CO}_2\text{R}$ . With mixed ethers, both iodides are formed, but mainly the one with the smaller radicle. Thus, of the two possible reactions with ethyl isoamyl ether,  $\text{Ph}\cdot\text{COI} + \text{Et}\cdot\text{O}\cdot\text{C}_5\text{H}_{11} = \text{Ph}\cdot\text{CO}_2\text{Et} + \text{C}_5\text{H}_{11}\text{I}$  and  $\text{Ph}\cdot\text{COI} + \text{Et}\cdot\text{O}\cdot\text{C}_5\text{H}_{11} = \text{Ph}\cdot\text{CO}_2\cdot\text{C}_5\text{H}_{11} + \text{EtI}$ , the second predominates. The same two reactions occur when ethyl isoamyl ether is treated with benzoyl chloride and potassium iodide, the predominating one being that in which ethyl iodide and isoamyl benzoate are formed.

T. H. P.

**Preparation of Acids and Amides by the Action of Ammonium Sulphide on Aliphatic Aromatic Ketones.** CONRAD WILLGERODT (*J. pr. Chem.*, 1909, [ii], 80, 183—191).—The paper gives an account of the amides and acids obtained since 1887 by the author's method of heating aliphatic aromatic ketones and yellow ammonium sulphide at a high temperature.

Ketone.	Temp.	Product.	M.p.
$\alpha$ -Naphthyl methyl ketone..	210—230°	$\alpha$ -Naphthylacetamide .....	—
"    ethyl    "	—	$\alpha$ -Naphthylpropionamide ...	140°
"    propyl   "	—	$\alpha$ -Naphthylbutyramide .....	160
<i>as-m</i> -Xylol methyl   "	—	<i>as-m</i> -Xylolacetamide .....	183
Cymyl methyl      "	270—300	Cymylacetamide .....	123
$\psi$ -Cumyl methyl     "	260—280	$\psi$ -Cumylacetamide .....	174
Mesityl methyl     "	260—280	Mesitylacetamide.....	208
—	—	<i>as-m</i> -Xylolbutyramide .....	123—124
—	—	<i>as-m</i> -Xylolpropionamide ..	107
<i>as-m</i> -Xylol isopropyl "	235—240	<i>as-m</i> -Xylolisobutyramide ...	120
—	—	<i>p</i> -Xylolbutyramide.....	125
<i>as-o</i> -Cymyl methyl   "	250	<i>as-o</i> -Cymylacetamide .....	112
$\beta$ -Naphthyl methyl   "	220—225	$\beta$ -Naphthylacetamide.....	200
"    ethyl    "	250—260	$\beta$ -Naphthylpropionamide ...	168
<i>p</i> -Tolyl methyl      "	250	<i>p</i> -Tolylacetamide.....	185
2-Bromo-5-tolyl methyl ketone .....	250—270	2-Bromo-5-tolylacetamide...	168
4-Bromo-3-tolyl methyl ketone .....	250—270	4-Bromo-3-tolylacetamide...	152
2-Chloro-5-tolyl methyl ketone .....	250—270	2-Chloro-5-tolylacetamide ...	162
4-Chloro-3-tolyl methyl ketone .....	250—270	4-Chloro-3-tolylacetamide ...	141

C. S.

**Preparation of Acids and Amides from Phenyl Alkyl Ketones by means of Yellow Ammonium Sulphide.** CONRAD WILLGERODT and FRANZ HUBERT MERK (*J. pr. Chem.*, 1909, [ii], 80, 192—200).—The authors find that the best conditions for the preparation of amides from ketones (preceding abstract) are to heat the ketone and yellow ammonium sulphide solution, in the proportion 1:5, for five to six hours at 200—220° in sealed glass tubes; the yellow ammonium sulphide solution is prepared by saturating con-

centrated ammonium hydroxide with hydrogen sulphide and dissolving 1 gram of sulphur per each 10 grams of the resulting liquid. When ammonium sulphide prepared from hydrogen sulphide and alcoholic ammonia is used, the reaction takes a somewhat different course, and hydrocarbons and arylthiophens are produced in addition to amides and acids. With regard to the limits within which the Willgerodt reaction is applicable, experiments on the ketones  $\text{Ph}\cdot\text{CO}\cdot\text{R}$ , where R is Me, Et,  $\text{Pr}^\alpha$ ,  $\text{Pr}^\beta$ ,  $\text{C}_4\text{H}_9$  (*iso*),  $\text{C}_6\text{H}_{13}$ , and  $\text{C}_{15}\text{H}_{31}$ , show that the yield of amide and acid decreases as the molecular weight of R increases. Thus phenyl methyl ketone gives 49.6% of phenylacetamide and 13.5% of phenylacetic acid, phenyl hexyl ketone gives 25% of heptamide and no acid, whilst phenyl pentadecyl ketone yields neither amide nor acid of the same carbon content as the original ketone.

C. S.

**Preparation of *o*-Nitro-derivatives of Nitriles.** KALLE & Co. (D.R.-P. 210563).—When *o*-nitrophenylpyruvic acid (10.5 parts) is dissolved in 100 parts of water and treated successively with a 10% solution of nitric acid (36.5 parts) and a concentrated solution containing 3.6 parts of sodium nitrite, *o*-nitrobenzonitrile slowly crystallises out.

F. M. G. M.

**Action of Silver Cyanide on Acetoxycarboxylic Chlorides.** RICHARD ANSCHÜTZ (*Annalen*, 1909, 368, 76—88).—An investigation on the transformation of acetoxycarboxylic chlorides into nitriles of  $\alpha$ -ketocarboxylic acids.

[With RUDOLF BÜCKER.]—*Acetoxypheylpyruvonitrile*,  
 $\text{OAc}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{CN}$ ,

is formed by heating acetylmandelyl chloride with silver cyanide at  $120^\circ$  for 2—3 hours; it crystallises in tufts of long, colourless needles, m. p.  $52.5^\circ$ , b. p.  $150$ — $151^\circ/10$  mm., and is converted by fuming hydrochloric acid into mandelic acid.

[With REINHOLD CLAUS.]—*o*-Acetoxypheylglyoxylonitrile,  
 $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CN}$ ,

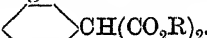
similarly prepared from acetylsalicylyl chloride, crystallises in long, stout plates, m. p.  $111$ — $112^\circ$ , b. p.  $149$ — $151^\circ/14$  mm.; measurements of the monoclinic crystals are given. It is converted by concentrated sulphuric acid or a solution of hydrochloric acid in glacial acetic acid into the corresponding amide,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$ , which crystallises in hard, small, white prisms, m. p.  $170^\circ$  (decomp.).

*o*-Acetoxypheylglyoxylic acid,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , cannot be obtained by treating the amide just described with nitrous acid, but is prepared by acting on this substance for several days with 38% hydrochloric acid at a temperature not above  $15^\circ$ ; it crystallises with  $1\text{H}_2\text{O}$  in fern-like aggregates of long, flat, colourless needles, m. p.  $101$ — $106^\circ$ ; the water is eliminated at  $90^\circ$ , yielding the anhydrous acid, m. p.  $134.5$ — $135.5^\circ$ . It is probable that the hydrated acid has the formula  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})_2\cdot\text{CO}_2\text{H}$ . The silver,  $\text{C}_{10}\text{H}_7\text{O}_5\text{Ag}$ , and sodium,  $\text{C}_{10}\text{H}_7\text{O}_5\text{Na}$ , salts are amorphous, white substances. The methyl ester,  $\text{C}_{11}\text{H}_{10}\text{O}_5$ , crystallises in white leaflets, m. p.  $109$ — $110^\circ$ . Attempts to obtain the lactone by heating the acid were unsuccessful.

W. H. G.

**Refractometric Researches.** JOHAN F. EYKMAN (*Chem. Weekblad*, 1909, 6, 699—712. Compare Abstr., 1908, ii, 1).—The refractometric constants of the following substances for the hydrogen and helium spectrum have been determined: *cyclohexane*, *cyclohexene*, *bromocyclohexane*, 1:2-dibromocyclohexane, ethyl malonate, ethyl ethanetetra-carboxylate, ethyl  $\Delta^2$ -cyclopentenemalonate, ethyl  $\Delta^2$ -cyclohexenemalonate, ethyl cyclohexylmalonate, cyclohexanecarboxylic acid, cyclopentylacetic acid, heptonic acid, cyclohexylacetic acid, cyclopenteneacetic acid, and cyclohexeneacetic acid.

*Ethyl  $\Delta^2$ -cyclohexenemalonate*,  $C_{13}H_{20}O_4$ , prepared by condensing ethyl disodiummalonate with dibromocyclohexene, has b. p.  $128^\circ/2$  mm.

$\Delta^2$ -cycloHexenemalononic acid, m. p. about  $165^\circ$ , loses carbon dioxide at this temperature, and yields  $\Delta^2$ -cyclohexeneacetic acid,  $C_8H_{12}O_2$ , m. p.  $11$ — $12^\circ$ , b. p.  $135$ — $136^\circ/14$  mm.,  $120^\circ/5$  mm. Its lactone has b. p. about  $250^\circ/760$  mm.,  $143^\circ/22$  mm. The amide has m. p.  $147$ — $148^\circ$ . Both acids readily decolorise an acetic acid solution of bromine and an alkaline solution of permanganate. The refractometric results accord with the  $\Delta^2$ -structure:   $CH(CO_2R)_2$ .

Bromocyclohexane and ethyl sodiomalonate yield ethyl cyclohexylmalonate,  $C_{13}H_{22}O_4$ , b. p.  $131$ — $133^\circ/16$  mm. cycloHexylmalonic acid has m. p. about  $180^\circ$  (decomp.) (compare Wallach, Abstr., 1907, i, 617).

*Ethyl cyclopentenemalonate*, prepared from chlorocyclopentene (compare Kraemer and Spilker, Abstr., 1896, i, 189) and ethyl sodiomalonate, has b. p.  $141^\circ/16$  mm. cycloPentenemalononic acid has m. p. about  $150^\circ$  (decomp.), and, on distillation under diminished pressure, yields cyclopenteneacetic acid,  $C_6H_7 \cdot CH_2 \cdot CO_2H$ , b. p.  $93$ — $94^\circ$ /about  $2.5$  mm., m. p.  $-19^\circ$ , which decolorises alkaline permanganate instantly, and combines with bromine in acetic acid solution to form a bromolactone, m. p.  $76^\circ$ . The amide of cyclopenteneacetic acid has m. p.  $131$ — $132^\circ$ . The constitution of the acid is probably

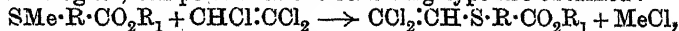
$CO_2H \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} : \text{CH} \end{smallmatrix}$  cycloPentylacetic acid,  $C_7H_{12}O_2$ , prepared

by reducing cyclopenteneacetic acid with nickel and hydrogen at  $170$ — $175^\circ$ , forms large leaflets, m. p.  $13$ — $14^\circ$ , b. p.  $133$ — $134^\circ/23$  mm. (Verwey, Abstr., 1896, i, 671, gives b. p.  $139$ — $140^\circ/26$  mm.). It does not decolorise either bromine or alkaline permanganate.

Dibromocyclohexene reacts with two molecules of ethyl sodiomalonate to form cyclohexene and ethyl ethanetetra-carboxylate, and not a cyclohexanedimalonic ester.

A. J. W.

**Preparation of Derivatives of Thiolbenzoic Acid.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 210644).—By the action of ethylene-trihalides (trichloroethylene, &c.) on the salts of thiolbenzoic acid and its homologues, compounds of the following type are obtained:



R being a simple or substituted benzene or naphthalene residue,  $R_1$  a metal, alkyl, or aryl group. The new substances are readily soluble in benzene or alcohol, but only sparingly so in petroleum or water.

*o*-Dichlorovinylthiolbenzoic acid,  $CO_2H \cdot C_6H_4 \cdot S \cdot CH \cdot CCl_2$ , forms

colourless crystals, m. p. 173°; its *ethyl* ester is a brown, viscous oil. *ω*-Dichloro-*p*-bromovinylthiolbenzoic acid forms colourless crystals, m. p. 188°. *ω*-Dichloro-*m*-ethoxyvinylthiolbenzoic acid has m. p. 155°. 1-*ω*-Dichlorovinylthiol-2-naphthoic acid is a yellow, crystalline powder, m. p. 174—175°. *ω*-Dibromovinylthiolbenzoic acid is a colourless, crystalline powder, m. p. 181°. F. M. G. M.

**Salts of Phenylthioglycolic [Thiolphenylacetic] Acid.** NICOLA PARRAVANO and G. TOMMASI (*Gazzetta*, 1909, 39, ii, 60—64).—Thiolphenylacetic acid (compare Ulpiani and Ciancarelli, *Abstr.*, 1904, i, 162) may be prepared by heating together mandelonitrile and a solution of hydrogen chloride saturated at 0°, in a sealed tube at 120—130°.

In aqueous solution the sodium salt has a molecular weight equal to one-half the calculated value, so that it undergoes dissociation into  $\text{SH}\cdot\text{CHPh}\cdot\text{CO}_2$  and Na. This aqueous solution dissolves the carbonates or hydroxides of cadmium, bismuth, copper, nickel, and cobalt; these metals cannot be detected in the liquids by the ordinary reagents. The cobalt compound,  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}_2\text{CoNa}_2\cdot 2\text{H}_2\text{O}$ , was obtained crystalline, and was found to have a molecular weight one-third of the calculated value in aqueous solution. It behaves, therefore, as the normally-dissociated sodium salt of cobaltothiophenylacetic acid,  $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{S}\cdot\text{Co}\cdot\text{S}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , a conclusion supported by conductivity measurements of the solution. T. H. P.

**Disengagement of the Formyl Group from Certain Aromatic Aldehydes.** CURIO M. MUNDICI (*Gazzetta*, 1909, 39, ii, 123—133).—When treated with hydrochloric acid,  $\beta$ -hydroxynaphthaldehyde readily loses the formyl group, but with chlorine or nitric acid it gives only substituted  $\beta$ -naphthols. When, however, its bispyrazolone derivative is boiled with dilute acid or alcohol, decomposition into  $\beta$ -naphthol and methylenebispyrazolone takes place (compare Betti and Mundici, *Abstr.*, 1907, i, 322).  $\beta$ -Methoxynaphthaldehyde exhibits similar behaviour, although to a less degree; with nitric acid it gives the methyl ether of a nitro- $\beta$ -naphthol and a nitroaldehyde, and with phenylmethylpyrazolone the bispyrazolone compound, decomposition of the latter with formation of methylene derivative only occurring on heating with dilute acid or in a sealed tube with alcohol. With phenylmethylpyrazolone, 2:4:6-trihydroxybenzaldehyde behaves in the cold like  $\beta$ -hydroxynaphthaldehyde, whilst 2:4:6-trimethoxybenzaldehyde gives a bispyrazolone derivative, which is readily resolved into trimethylphloroglucinol and methylpyrazolone by dilute acids.

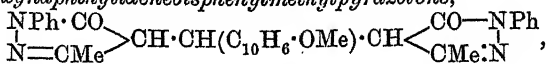
The instability of the aldehyde group in  $\beta$ -hydroxynaphthaldehyde is hence not peculiar to the naphtholic derivative, but is inherent to the nature and position of the substituents.

The action of chlorine on  $\beta$ -hydroxynaphthaldehyde yields the tetrachloro- $\beta$ -ketohydronaphthol obtained by Zincke (*Abstr.*, 1889, 265) by the action of chlorine on  $\beta$ -naphthol in acetic acid solution. The action of nitric acid gives 1:6-dinitro- $\beta$ -naphthol.

An improved method is given for the preparation of  $\beta$ -methoxy-

naphthaldehyde (compare Rousset, Abstr., 1898, i, 591). The action of nitric acid on this compound yields: (i) a nitro- $\beta$ -methoxynaphthaldehyde,  $C_{12}H_9O_4N$ , which forms crystals, m. p.  $174^\circ$ : its constitution was not determined; (2) the methyl ether of 1-nitro- $\beta$ -naphthol,  $C_{11}H_9O_3N$ , which crystallises from benzene in lemon-yellow plates, m. p.  $126^\circ$ .

*$\beta$ -Methoxynaphthylidenebisphenylmethylpyrazolone,*



prepared from phenylmethylpyrazolone and  $\beta$ -methoxynaphthaldehyde, forms white needles, m. p.  $195^\circ$ , and is soluble in dilute alkali solution and in concentrated sulphuric acid, giving a yellow coloration. This compound is accompanied by  *$\beta$ -methoxynaphthylidenephenylmethylpyrazolone,*

*pyrazolone,*  $\begin{array}{c} \text{NPh} \cdot \text{CO} \\ | \\ \text{N} = \text{CMe} \end{array} > \text{C} \cdot \text{CH} \cdot \text{C}_{10}\text{H}_6(\text{OMe})$ , which crystallises in

aggregates of small needles, m. p.  $219.2^\circ$ , and gives an intense red coloration with concentrated sulphuric acid. When boiled in alcoholic solution, this compound is converted into an isomeride, which crystallises in slender, yellowish-red prisms, m. p.  $135^\circ$ , and in alcoholic solution in presence of a few crystals of the original compound, m. p.  $219.2^\circ$ , is converted into the latter.

The *bispyrazolone* derivative of 2:4:6-trimethoxybenzaldehyde,  $C_{30}H_{30}O_5N_4$ , crystallises in mammillary aggregates of white needles, m. p.  $204^\circ$ .

T. H. P.

**Condensation of Aminohydroxy-acids with Aromatic Aldehydes.** III. and IV. ERNESTO PUXEDDU (*Gazzetta*, 1909, 39, ii, 21—32, 32—43).—The following results have been obtained in continuance of the author's previous work (Abstr., 1908, i, 286; this vol., i, 238).

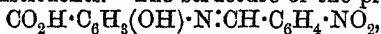
6-Amino-*m*-hydroxybenzoic acid condenses with the three nitrobenzaldehydes to give compounds, all of which have the formula  $C_{14}H_{10}O_5N_2$ ; that from *o*-nitrobenzaldehyde crystallises in golden-yellow, prismatic needles, decomposing at  $220^\circ$ ; that from the meta compound crystallises in greenish-yellow, six-faced prisms, decomposing at above  $240^\circ$ , and that from the para forms greenish-yellow, prismatic needles, decomposing at above  $240^\circ$ . The same acid gives with salicylaldehyde the compound,  $C_{14}H_{11}O_4N$ , which separates in yellow needles, decomposing at  $248^\circ$ ; with *p*-hydroxybenzaldehyde, a mixture of two compounds, one golden-yellow and the other dark red; with anisaldehyde, the compound,  $C_{15}H_{13}O_4N$ , which crystallises in yellow, silky needles, m. p.  $227.8^\circ$ ; with catechualdehyde, a brown, crystalline powder, which is almost insoluble in all the organic solvents and was not analysed, and with vanillaldehyde, the compound,  $C_{15}H_{13}O_5N$ , m. p.  $267^\circ$  (decomp.), which is apparently a mixture of red and yellow crystals and, when dissolved in alcohol, exhibits feeble blue fluorescence.

5-Aminosalicylic acid gives with *o*-nitrobenzaldehyde the compound,  $C_{14}H_{10}O_5N$ , which crystallises from alcohol in yellow, prismatic needles, m. p.  $223^\circ$  (decomp.); with *p*-hydroxybenzaldehyde, the compound,

$C_{14}H_{11}O_4N$ , which forms orange-yellow, prismatic needles, decomposing at  $240-260^\circ$ , and when dried in an oven assumes a dark red colour and exhibits a blue reflection; on pouring into water, it again becomes orange-coloured and shows green reflection.

The same acid gives with anisaldehyde a small quantity of a reddish-yellow, crystalline substance, which was not analysed, and with catechualdehyde, the compound,  $C_{14}H_{11}O_5N$ , a brownish-green powder.

Hydrolysis of the condensation product of 6-amino-*m*-hydroxybenzoic acid and *o*-nitrobenzaldehyde by means of dilute hydrochloric acid yields the two constituents. The structure of the product is hence



the  $H_2$  of the amino-group and the  $O$  of the aldehydic group being eliminated in the condensation. The hydrochloride of the condensation product,  $C_{14}H_{10}O_5N_2 \cdot HCl$ , prepared by the action of fuming hydrochloric acid, forms transparent crystals.

*Amino-m-cresotic acid hydrochloride*,  $C_8H_9O_3N \cdot HCl$ , separates in colourless, prismatic needles, m. p.  $263^\circ$  (decomp.). The condensation product obtained from amino-*m*-cresotic acid and *o*-nitrobenzaldehyde behaves towards concentrated or dilute hydrochloric acid in the same manner as the product given by 6-amino-*m*-hydroxybenzoic acid and *o*-nitrobenzaldehyde.

In addition to hydrochlorides, these condensation products form sodium salts, which can be obtained crystalline.

Many of the condensation products exhibit fluorescence, in some cases in alcoholic solution, and in others in acid or alkaline solution. It is probable that the fluorescence is connected with the presence of the group  $\cdot CH : N \cdot$ , which has a fluorogenic character intermediate between those of the groups  $\cdot CH : CH \cdot$  and  $\cdot N : N \cdot$ .

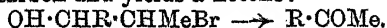
In some instances these condensation products appear to exist in two forms, which are probably the stereoisomerides rendered possible by the presence in the molecule of a carbon atom doubly linked to a nitrogen atom.

In general, the capacity of an aldehyde for reacting with amines increases with an increase in the negative character of the substituent groups in its molecule. The double linking of cinnamaldehyde also appears to stimulate the activity of the aldehyde in this respect.

A table is given showing the degrees of readiness with which the four amino-acids—5-aminosalicylic, 6-amino-*m*-hydroxybenzoic, and amino-*o*- and amino-*m*-cresotic—react with the twelve aldehydes examined.

T. H. P.

**Formation of Acetophenones from Derivatives of Propylbenzene.** EFISIO MAMELI [with RAIMONDO BONU and CESARE BIGNAMI] (*Gazzetta*, 1909, 39, ii, 165—172. Compare this vol., i, 714).—When a  $\beta$ -bromo- $\alpha$ -hydroxydihydro-derivative of an aromatic olefine containing the propenyl group is oxidised, either by chromic acid or by boiling with hydrochloric acid under a reflux condenser, it loses an atom of carbon and yields a ketone:



For the occurrence of this reaction, which furnishes a new method of preparation of acetophenones, it is necessary that the compound em-

played should not contain double linkings and that the hydroxyl group should be in the  $\alpha$ -position and the bromine atom in the  $\beta$ -position. If one of these conditions is not observed, a ketone is obtained with all three carbon atoms in the side-chain (compare Hell, Abstr., 1896, i, 169; Hell and Gärtner, Abstr., 1895, i, 341; Hell and von Günther, Abstr., 1896, i, 20; Hoering, Abstr., 1904, i, 577; 1905, i, 902; Balbiano, Abstr., 1906, i, 186; 1907, i, 522; Tiffeneau and Daufresne, Abstr., 1907, i, 701; Mameli, Abstr., 1904, i, 1023).

$\beta$ -Bromo- $\alpha$ -hydroxydihydroisosafrrole, under the above conditions, yields acetylpipecrone (compare Feuerstein and Heimann, Abstr., 1901, i, 465), whilst  $\beta$ -bromo- $\alpha$ -hydroxydihydroanethole gives *p*-methoxyacetophenone,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COMe}$ , as a greenish-yellow oil, b. p. 185—190°/120 mm., difficult to purify from traces of bromo-derivative (Eykmann, Bergema, and Henrard, Abstr., 1905, i, 361, give m. p. 35°); the *semi-bazone* has m. p. 181—182°.

T. H. P.

Transformation of 4:4':4'':4'''-Tetrachlorobenzopinacolone into  $\beta$ -4:4':4'':4'''-Tetrachlorobenzopinacolin and the Velocity of the Reaction. PIETER A. MEERBURG (*Rec. trav. chim.*, 1909, 28, 267—269).—It has been shown previously (*ibid.*, 1905, 24, 131) that, making certain assumptions, the transformation of 4:4':4'':4'''-tetrachlorobenzopinacolone into the  $\beta$ -pinacolin by acetyl chloride at 70° is probably a unimolecular reaction, intermediate products not being formed. At 30°, however, it was observed that the quantity of  $\beta$ -pinacolin formed increased with the time to a maximum, then diminished to a minimum, and then rapidly increased again. The experiments at 30° have been repeated, certain improvements having been made in the method employed. The results do not give the characteristic curves obtained previously, but trustworthy conclusions cannot be drawn from them, since among the values calculated for the constant ( $K$ ), assuming the reaction to be unimolecular, one or more occur widely different from the rest. The cause of these deviations was not discovered.

E. H.

Transformation of  $\alpha$ -4:4':4'':4'''-Tetrachlorobenzopinacolin into  $\beta$ -4:4':4'':4'''-Tetrachlorobenzopinacolin and the Velocity of the Reaction. PIETER A. MEERBURG (*Rec. trav. chim.*, 1909, 28, 270—271. Compare Montagne, Abstr., 1907, i, 141).— $\beta$ -4:4':4'':4'''-Tetrachlorobenzopinacolin when heated with alcoholic potassium hydroxide solution is decomposed into 4:4':4''-trichlorotriphenylmethane and potassium *p*-chlorobenzoate. Accordingly, the rate of change of the  $\alpha$ - into the  $\beta$ -pinacolin was measured by heating the alcoholic solution of the reaction products (after increasing periods of time) with known amounts of potassium hydroxide dissolved in alcohol, and estimating the alkali used. From the experimental results the values of the constant  $K$ , calculated on the assumption that the change is a unimolecular one, indicate that this assumption is justified, and that accordingly the transformation of the  $\alpha$ - into the  $\beta$ -pinacolin is an intramolecular reaction.

E. H.

Intramolecular Atomic Migrations. IX. Conversion of  $\alpha$ -Glycols into Aldehydes. P. J. MONTAGNE (*Rec. trav. chim.*, 1909, 28, 272—275. Compare Abstr., 1905, i, 445).—Tiffeneau supports

the view that in the transformation of  $\alpha$ -glycols into the corresponding aldehydes, intermediate compounds, probably diethylene oxides, are formed (Abstr., 1908, i, 165).

The determinations made by Meerburg (preceding abstracts) of the rate of change of tetrachlorobenzopinacolone into  $\beta$ -tetrachlorobenzopinacolin agree with the formula for a unimolecular reaction. The transformation can therefore only proceed through the formation of an intermediate compound ( $\alpha$ -4 : 4' : 4'' : 4'''-tetrachlorobenzopinacolin) if one or other of the two changes involved proceeds with relatively very great velocity. Meerburg has shown that the change of the  $\alpha$ - into the  $\beta$ -pinacolin is not a rapid one, and an experiment made by the author showed that after thirty minutes' heating with acetyl chloride at 70° the greater proportion of the tetrachlorobenzopinacolone remains unchanged, indicating that the first assumed change is not more rapid. The conclusion is drawn that the transformation of the pinacolone into the  $\beta$ -pinacolin does not involve the formation of the intermediate  $\alpha$ -pinacolin, and therefore is not in accordance with Tiffeneau's hypothesis. E. H.

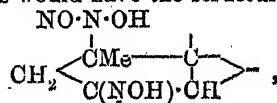
**Action of Sulphuric Acid on Santonin.** I. GUIDO BARGELLINI and A. MANNINO (*Gazzetta*, 1909, 39, ii, 101—105).—According to Andreocci and Bertolo (Abstr., 1899, i, 301), the action of hydrochloric acid on santonin yields desmotroposantonin,  $[\alpha]_D + 112^\circ$ , whilst that of sulphuric acid (D 1.44) gives *l*-desmotroposantonin,  $[\alpha]_D - 140^\circ$ .

The authors find, however, that these two acids do not exert specific actions on santonin. For, if sulphuric acid (D 1.44) acts on santonin at a low temperature, *l*-desmotroposantonin is formed, whilst at a high temperature the *d*-form,  $[\alpha]_D + 112^\circ$ , is obtained.

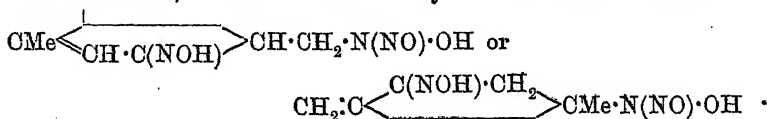
It is further shown that *l*-desmotroposantonin, and also *isodesmotroposantonin*, m. p. 188°,  $[\alpha]_D + 129^\circ$ , are converted by the action of sulphuric acid (D 1.44) into desmotroposantonin,  $[\alpha]_D + 112^\circ$ , which is therefore the stable form.

Under the conditions which result in the formation of *isodesmotroposantonin* from desmotroposantonin (heating with potassium hydroxide at 210°), *l*-desmotroposantonin remains unchanged. T. H. P.

**Hydroxylamineoximes of Santonin.** III. LUIGI FRANCESCONI and GUIDO CUSMANO (*Gazzetta*, 1909, 39, ii, 105—115).—The authors have examined further  $\alpha$ - and  $\beta$ -hydroxylaminosantoninoximes and their derivatives (see Abstr., 1908, i, 272), in particular the action on them of nitrous acid (compare following abstract). The nitroso-compounds obtained are nitrosohydroxylamines and not pernitroso-compounds, the hydroxylamino-group being attacked by nitrous acid in preference to the oxime grouping. They give intense Liebermann's reactions, are soluble in alkali hydroxide solution, and are readily decomposed in the cold by mineral acids and in the hot by acetic acid, yielding alcohol-oximes by the replacement of the group  $N_2O_2H$  by OH. On the basis of Angeli and Marino's constitution for santonin, these nitroso-compounds would have the structure :



whilst according to the authors' formula for santonin, they would have one of the two following structures if the  $\alpha$ - and  $\beta$ -compounds are stereoisomerides, or both of them if they are structural isomerides:



Attempts were made to eliminate the oxime grouping from these compounds in order to ascertain whether a saturated tertiary ketonic alcohol (Angeli and Marino's formula) is formed, or either a primary ketonic alcohol or an unsaturated tertiary ketonic alcohol (authors' formula). It is found, however, that these oxime-alcohols only partly lose hydroxylamine, giving resinous products; in preference to such change, dehydration and molecular rearrangement occur, the product being, for both the  $\alpha$ - and  $\beta$ -compounds, a single compound,  $\text{C}_{15}\text{H}_{19}\text{O}_8\text{N}$ , which contains the group  $\cdot\text{CO} \cdot \text{NH} \cdot$ , but no oxime or nitrile group, and is possibly a lactam derived from the oxime by Beckmann's transformation. From this ready elimination of water, it is concluded that both the oxime-alcohols contain a tertiary alcoholic group, and that the  $\alpha$ - and  $\beta$ -compounds are stereoisomerides.

$\alpha$ -Hydroxylaminosantoninoxime has  $[\alpha]_D^{25} + 47.41^\circ$ . Its *hydrochloride*,  $\text{C}_{15}\text{H}_{22}\text{O}_4\text{N}_2 \cdot \text{HCl}$ , crystallises in massive prisms or minute needles, m. p.  $212^\circ$  (decomp.).

$\beta$ -Hydroxylaminosantoninoxime has  $[\alpha]_D^{25} - 3.00^\circ$ . The *hydrochloride*,  $\text{C}_{15}\text{H}_{22}\text{O}_4\text{N}_2 \cdot \text{HCl}$ , forms shining, flattened, pentagonal crystals, m. p.  $163^\circ$  (decomp.).

Hydroxylammoniohydroxylaminosantoninoxime has  $[\alpha]_D^{25} + 8.97^\circ$ .

T. H. P.

Nitrosohydroxylaminosantoninoximes and their Derivatives. IV. LUIGI FRANCESCOINI and GUIDO CUSMANO (*Gazzetta*, 1909, 39, ii, 115—123. Compare preceding abstract).—Oxidation of  $\beta$ -hydroxylaminosantoninoxime by means of mercuric oxide or ferric chloride yields a reddish-yellow powder,  $\text{C}_{15}\text{H}_{20}\text{O}_5\text{N}_2$ , which reduces Fehling's solution, dissolves in acids or alkalis, begins to blacken at  $200^\circ$ , and decomposes completely at about  $230^\circ$ . If the oxidation is effected by means of permanganate, a substance is obtained having the same composition and properties as the above, with the exception that it decomposes completely at  $200^\circ$ .

Oxidation of  $\alpha$ -hydroxylaminosantoninoxime yields a pale yellow powder, decomposing at about  $240^\circ$ .

Reduction of the two hydroxylaminosantoninoximes by various means led to no definite products.

Nitroso- $\beta$ -hydroxylaminosantoninoxime,  $\text{C}_{15}\text{H}_{21}\text{O}_5\text{N}_3$ , crystallises in yellow prisms, decomposing at  $160$ — $172^\circ$ , and is converted by the action of acetic acid into

$\beta$ -Hydroxysantoninoxime,  $\text{C}_{15}\text{H}_{21}\text{O}_4\text{N}$ , which forms tufts of white, silky prisms, softening at  $175^\circ$  and evolving gas at  $195^\circ$ , and dissolves in the cold in acids or alkali hydroxide solutions, giving liquids which only reduce Fehling's solution after boiling;  $[\alpha]_D^{25} + 126.8^\circ$ .

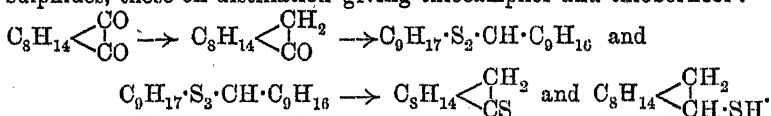
*Nitroso- $\alpha$ -hydroxylaminosantoninoxime*,  $C_{15}H_{21}O_5N_3$ , crystallises in tufts of white, feathery needles, which turn yellow at  $100^\circ$  and decompose at  $164^\circ$ ;  $[\alpha]_D^{25} -112.8^\circ$ .

*$\alpha$ -Hydroxysantoninoxime*,  $C_{15}H_{21}O_4N$ , crystallises in large, pyramidal prisms, m. p.  $199-200^\circ$ ,  $[\alpha]_D^{25} +219.6^\circ$ .

The *lactam* compound,  $C_{15}H_{19}O_3N$ , obtained by the action of dilute hydrochloric acid or sodium hydroxide solution on either  $\alpha$ - or  $\beta$ -hydroxysantoninoxime, crystallises in shining, rectangular plates, which turn yellow at  $200^\circ$  and decompose rapidly at  $250^\circ$ . When boiled with 10% sodium hydroxide solution, this lactam yields a small quantity of a nitrogenous compound, containing 62.61% C and 7.65% H, and crystallising in long, hard prisms, which soften at  $190^\circ$  and decompose rapidly at  $230^\circ$ ; this compound gives an aqueous solution which has an acid reaction towards litmus, and when heated at  $180^\circ$  for some time yields the original lactam,  $C_{15}H_{19}O_3N$ . T. H. P.

**New Researches in the Camphor Group. III. ENRICO RIMINI** (*Gazzetta*, 1909, 39, ii, 196—212. Compare this vol., i, 728).—The action of concentrated sulphuric acid on tanacetone or pernitrosotanacetone yields *isotanacetone*, which is more readily prepared by this reaction than by Wallach and Scharfenberg's method (*Abstr.*, 1895, i, 620). Tanacetone, when heated, is converted into *carvotanacetone*, whilst by the action of hot 50% sulphuric acid, or cold concentrated sulphuric acid, it yields *isotanacetone*; *carone*, on the other hand, gives one and the same product, namely, *carvenone*, when heated or when treated in the cold with concentrated sulphuric acid.

Camphorquinone, when gradually heated to  $150^\circ$  in a sealed tube with solid ammonium hydrosulphide and alcohol, is first reduced to camphor, part of which reacts with the excess of ammonium hydrosulphide, yielding a mixture consisting principally of bornyl di- and trisulphides, these on distillation giving thiocamphor and thioborneol:



The behaviour of fenchone towards ammonium hydrosulphide is quite similar to that of camphor, the product of the reaction being *thiofenchone*,  $C_{10}H_{16}S$ , which is obtained as a red oil, b. p.  $207-208^\circ/734$  mm., m. p.  $24^\circ$ . When reduced with aluminium amalgam, thiofenchone yields *thiofenchyl alcohol*, b. p.  $206^\circ/732$  mm., m. p.  $24^\circ$ , which, with mercuric acetate, gives the *mercury mercaptide*,  $C_{20}H_{34}S_2Hg$ , crystallising in white, silky needles, m. p.  $149^\circ$ . With semicarbazide, phenylhydrazine, or hydroxylamine, thiofenchone yields the semicarbazone, hydrazone, or oxime of fenchone.

The thioterpenones of the camphor series may be readily prepared by heating the pernitrosoterpenones with ammonium hydrosulphide on the water-bath, the reaction:  $>CN_2O_2 + H_2S = >CS + N_2O + H_2O$ , being analogous to that effected by dilute acid or alkali:  $>CN_2O_2 + H_2O = >CO + N_2O + H_2O$ .

Thiocamphor, prepared in this way from pernitrosocamphor, has

m. p. 136°, and the mercury mercaptide corresponding with thioborneol, 175° (compare Wuyts, Abstr., 1903, i, 428). Accompanying the thio-camphor is a substance,  $C_{40}H_{68}S_6$ , m. p. 178—179°, probably identical with the pentasulphide, m. p. 183—185°, obtained by Wuyts (*loc. cit.*). The mercaptide of thioborneol, obtained from camphorquinone, has m. p. 153°, the higher m. p. of the product prepared from pernitroso-camphor being unexplained.

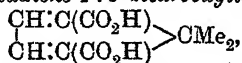
The action of ammonium hydrosulphide on pernitrosofenchone yields thiofenchone as principal product, and small proportions of fenchone and of a sulphur-containing oil, presumably composed of a mixture of polysulphides. Further, pernitrosomenthone gives a mixture of menthone and thiomenthone, and tanacetone yields thioisotanacetone.

T. H. P.

**Syntheses in the Camphor and Terpene Series. I. Complete Synthesis of *apo*Camphoric Acid and its Derivatives.** GUSTAV KOMPPA (*Annalen*, 1909, 368, 126—155).—Many unsuccessful attempts to synthesise *apocamphoric* acid are briefly mentioned, whilst the method which led finally to the complete synthesis of this compound is described in detail. A short account of this work has already appeared (compare Abstr., 1901, i, 668). The following are the compounds which have not been described in detail hitherto.

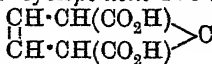
Methyl diketoapocamphorate (1 mol.), when treated with hydroxylamine hydrochloride (2 mols.) and potassium carbonate (1 mol.) in aqueous methyl alcohol, yields the *oxime*,  $C_{11}H_{15}O_6N$ , which crystallises in small, flat, white needles, m. p. 149—150°.

2:2-Dimethylcyclopentadiene-1:3-dicarboxylic acid,



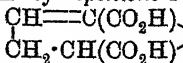
may be prepared from 4:5-dihydroxyapocamphoric acid (1) by distillation under 25 mm. pressure; (2) by boiling with 45% sulphuric acid or 10% hydrochloric acid; (3) by heating with anhydrous oxalic acid at 120—130°. It crystallises in rosettes of flat needles, m. p. 242—243°.

2:2-Dimethyl- $\Delta^4$ -cyclopentene-1:3-dicarboxylic acid (*isodehydroapocamphoric acid*),



is prepared by reducing 4:5-dihydroxyapocamphoric acid with sodium amalgam or hydriodic acid and red phosphorus. It crystallises in triclinic plates or flat, pointed needles, m. p. 208—209.5°. The *anhydride*,  $C_9H_{10}O_3$ , prepared by the action of acetyl chloride or acetic anhydride on the acid, forms crystalline nodules, m. p. 193—195°.

2:2-Dimethyl- $\Delta^6$ -cyclopentene-1:3-dicarboxylic acid (*dehydroapocamphoric acid*),



results from the action of aqueous sodium hydroxide on  $\beta$ -bromoapocamphoric acid; it crystallises in long needles, m. p. 223—224°.

W. H. G.

**Terpenes and Etheral Oils.** C. OTTO WALLACH (*Annalen*, 1909, 368, 1—22. Compare this vol., i, 383).—I. *Synthesis of*

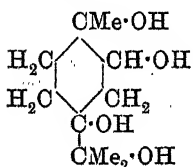
*Active  $\alpha$ -Pinene from Nopinone.*—When nopinolacetic acid is submitted to slow, dry distillation in a current of hydrogen it yields a mixture of *l*- $\alpha$ -pinene, *l*- $\beta$ -pinene, and fenchene (compare Abstr., 1908, i, 997); the fraction which passes over below  $165^\circ$  is composed almost entirely of the isomeric pinenes, and contains about 10% of the  $\alpha$ -compound. The presence of *l*- $\alpha$ -pinene was established by carefully oxidising the mixture of isomerides by means of 1% potassium permanganate solution, whereby it was possible to detect *l*-pinonic acid (compare Barbier and Grignard, Abstr., 1908, i, 852) among the oxidation products.

When nopinolacetic acid is distilled with acetic anhydride it yields  $\beta$ -pinene and an acid,  $C_{13}H_{22}O_5$ , which crystallises in needles, m. p.  $58-59^\circ$ , sublimes when heated rapidly, and behaves as a saturated compound towards permanganate. It loses 1 mol. of acetic acid when boiled with aqueous sodium hydroxide, yielding the acid, m. p.  $85-86^\circ$ , obtained previously (Abstr., 1908, i, 998) by heating nopinolacetic acid with potassium hydrogen sulphate.

$\beta$ -Pinene, when treated with 3% sulphuric acid or a mixture of equal parts of alcohol and nitric acid (D 1.255), is converted into terpene hydrate.

The formula assigned to the glycol, m. p.  $75-77^\circ$ , obtained from  $\beta$ -pinene (Abstr., 1908, i, 999) is shown to be correct, since this substance when oxidised by a 1% aqueous solution of potassium permanganate at  $0^\circ$  is converted into nopic acid.

II. *The Erythritol of Terpinolene.*—Terpinolene is most readily obtained by the action of anhydrous formic acid on  $\gamma$ -terpineol.



When oxidised by potassium permanganate it yields *terpinolene erythritol*, m. p.  $149-150^\circ$ , having the annexed formula; the substance also crystallises with  $1\text{H}_2\text{O}$  in hard, well-defined crystals, which sinter at  $90^\circ$ , m. p.  $100-130^\circ$  (decomp.). It is thus definitely established that the erythritol obtained from ordinary terpinene is not derived from terpinolene (compare Abstr., 1908, i, 813).

The product obtained by the dry distillation of anhydrous dihydrocarvylamine hydrochloride contains but a very small quantity of "terpinene," whilst that derived from the phosphate by similar treatment is composed almost entirely of  $\alpha$ -terpinene.

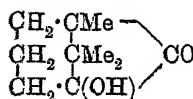
Chlorocarvenene, likewise the hydrocarbon derived from it by reduction (compare Semmler, this vol., i, 110), are shown to belong to the terpinene series, since they both yield  $\alpha\alpha'$ -dihydroxy- $\alpha$ -methyl- $\alpha'$ -isopropyladipic acid when oxidised. It is made evident, however, that a relatively pure chloroterpinene (chlorocarvenene) can only be obtained with the greatest difficulty by the action of phosphorus pentachloride on carvenone. The density of the chloro-compound cannot be greatly removed from 1 (compare Semmler, *loc. cit.*; Klages and Kraith, Abstr., 1900, i, 42).

[With ERICH GROSSE.]—III. *The Sesquiterpene Present in Siberian Pine-oil.*—A *sesquiterpene*,  $C_{15}H_{24}$ , has been isolated from Siberian pine-oil, having b. p.  $260-268^\circ/760$  mm. (slight decomp.),  $D_{20}^{25} 0.8725$ ,  $n_D^{20} 1.4903$ . The trihydrochloride,  $C_{15}H_{24}\cdot 3\text{HCl}$ , crystallises in colour-

less needles, m. p. 79—80°; the trihydrobromide,  $C_{15}H_{21} \cdot 3HBr$ , has m. p. 84°. It is probable, therefore, that three ethylene linkings are present in the sesquiterpene, although only four atoms of bromine combine immediately with the hydrocarbon.

The hydrochloride is undoubtedly identical with limene trihydrochloride (compare Burgess and Page, *Trans.*, 1904, 85, 414); it has not been established whether the hydrocarbon itself is identical with limene or the sesquiterpene obtained from opoponax-oil (Schimmel & Co., *Abstr.*, 1904, i, 603). W. H. G.

**Biological Oxidation of Carone and Fenchone. II.** ENRICO RIMINI (*Gazzetta*, 1909, 39, ii, 186—196. Compare *Abstr.*, 1901, i, 393; ii, 522).—When carone is administered by ingestion to a dog and the urine is boiled with dilute sulphuric acid, carvacrol is obtained. Hence in the animal organism the carone undergoes oxidation to hydroxycarone (compare von Baeyer and Baumgärtel, *Abstr.*, 1899, i, 223), which is eliminated in the urine as caroneglycuronic acid; by boiling with dilute sulphuric acid, the latter yields successively hydroxycarone, ketoterpene, and carvacrol. Consequently carone is not hydrolysed, but oxidised, in the animal organism. Cryoscopic comparison of oxyfenchone (*loc. cit.*) with hydroxycamphor indicates that the former is a keto-alcohol, and its resistance to permanganate in the cold, and the fact that it is not oxidised by Beckmann's chromic mixture to give a diketone, point to its being a saturated tertiary alcohol. According to Glover's formula for fenchone (*Trans.*, 1908, 93, 1285), hydroxyfenchone would have the annexed structure, which appears to the author to be the most probable one.



Fenchonephenylhydrazone, b. p. 202—203°/18 mm., may be prepared by the action of phenylhydrazine acetate on pernitrosofenchone.

T. H. P.

**Chemistry of Hops.** RUD. SILLER (*Zeitsch. Nahr. Genussm.*, 1909, 18, 241—271).—By extracting the lupulin of hops with ether, evaporating the solvent, dissolving the residue in methyl alcohol, and precipitating by means of methyl-alcoholic lead acetate, the author obtains a lead salt of the  $\alpha$ -bitter acid, which, when crystallised from acetic acid, corresponds with the formula  $(C_{20}H_{31}O_5Pb)_2O$ . He is, however, inclined towards the formula  $C_{20}H_{30}O_5Pb$  (compare Barth, *Abstr.*, 1900, ii, 746; 1901, i, 40), the discrepancy in the analytical numbers being ascribed to the ready formation of basic salts and to the presence of traces of resin. The factor for converting the lead salt into free  $\alpha$ -acid is 0.6319. In precipitating the lead salt, excess of the precipitant is to be avoided, as it dissolves the precipitate, apparently with formation of basic salts. Traces of the  $\alpha$ -acid hence give only a yellow coloration with methyl-alcoholic lead acetate. A method of procedure for the complete precipitation of the  $\alpha$ -acid is described.

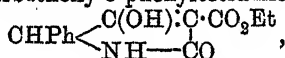
In order to obtain the pure crystallised  $\alpha$ -acid, the lead salt is recrystallised once from glacial acetic acid and then decomposed with dilute sulphuric acid and ether. The pure  $\alpha$ -acid is extremely resistant

to chemical reagents, but it is rapidly transformed into a resin by heating at a high temperature, absorption of oxygen taking place. Impure  $\alpha$ -acid undergoes slow autoxidation. The  $\alpha$ -acid contains at least two double linkings, since the molecule unites with four atoms of bromine, giving the compound  $C_{20}H_{32}O_5Br_4$ . When extracted with light petroleum, disintegrated hops yield far greater amounts of bitter substances than the whole hops.

The  $\gamma$ -resin, generally supposed to be an individual substance, is found to be a mixture of at least two different resins, differing in carbon-content and in solubility in ether.

T. H. P.

**The Tetrionic Acid Group. II. Action of Acetylmandelyl Chloride on Ethyl Sodiomalonate and Ethyl Sodiocynoacetate.** RICHARD ANSCHÜTZ and RUDOLF BÖCKER (*Annalen*, 1909, 368, 53—75. Compare Anschütz and Bertram, *Abstr.*, 1903, i, 271).—Acetylmandelyl chloride, similarly to acetylsalicyl chloride (compare this vol., i, 660), condenses with ethyl sodiomalonate, yielding 3-carbethoxy-5-phenyltetronic acid, from which 5-phenyltetronic acid is obtained on treatment with aqueous potassium hydroxide. Condensation with ethyl sodiocynoacetate leads to the formation of ethyl acetylphenylglycolyl- $\alpha$ -cyanoacetate,  $OAc \cdot CHPh \cdot CO \cdot CH(CN) \cdot CO_2Et$ , but, unlike the analogous ethyl *o*-acetoxybenzoyl- $\alpha$ -cyanoacetate (*loc. cit.*), this compound, when boiled with ethyl or methyl alcohol, or when treated with cold concentrated hydrochloric acid, yields a substance which is possibly 3-carbethoxy-5-phenyltetramic acid,



or, since it does not possess acidic properties, more probably  $\alpha$ -carbethoxy- $\beta$ -keto- $\gamma$ -phenylbutyrolactam,  $CHPh \begin{array}{l} \diagup CO - CH \cdot CO_2Et \\ \diagdown NH - CO \end{array}$ .

Attempts to prepare the acid corresponding with this ester by hydrolysing with alkali led to the isolation of two isomeric acids. The relationship existing between these acids and the parent substance is not yet clear.

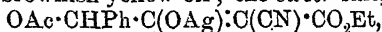
*Acetylmandelic acid*,  $OAc \cdot CHPh \cdot CO_2H$ , prepared by the action of acetyl chloride on mandelic acid, crystallises with  $1H_2O$  in slender needles, which effloresce when kept in the air; the anhydrous acid has m. p.  $80^\circ$ ; the *ammonium* salt,  $C_{10}H_{13}O_4N$ , crystallises in glistening, white scales; the *chloride*,  $C_{10}H_9O_3Cl$ , is a colourless, oily liquid, b. p.  $129^\circ/10$  mm.,  $132^\circ/12$  mm.,  $142^\circ/18$  mm.; the *amide*,  $C_{10}H_{11}O_3N$ , forms tufts of slender, white needles, m. p.  $112$ — $113^\circ$ ; the *anilide*,  $C_{16}H_{15}O_3N$ , crystallises in slender, white needles, m. p.  $117.5^\circ$ ; the *p*-phenetide,  $C_{18}H_{19}O_4N$ , forms small, slender, white needles, m. p.  $157^\circ$ ; the *piperide*,  $C_{15}H_{19}O_3N$ , crystallises in glistening, white needles, m. p.  $98^\circ$ .

*3-Carbethoxy-5-phenyltetronic acid*,  $CHPh \begin{array}{l} \diagup C(OH) : C \cdot CO_2Et \\ \diagdown O - CO \end{array}$ , crystallises in small, white needles, m. p.  $140^\circ$ ; the *ammonium* salt, a white powder; *sodium* salt,  $C_{12}H_{11}O_5Na$ ; *ferric* salt,  $(C_{12}H_{11}O_5)_3Fe$ , a bright red powder, and *cobalt* salt,  $(C_{12}H_{11}O_5)_2Co$ , small, dark red

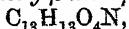
crystals, were analysed; the crystalline *nickel*, *lead*, *magnesium*, and *copper* salts were also prepared.

5-Phenyltetronic acid,  $\text{CHPh} \begin{array}{c} \text{C(OH):CH} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{array}$ , crystallises in feathery aggregates of felted, white needles, m. p. 127.5—128.5°; the ammonium salt,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$ , forms white, stellate scales, m. p. 148—149° (decomp.); the sodium salt,  $\text{C}_{10}\text{H}_9\text{O}_3\text{Na}$ , has m. p. 105—110°. The acid is converted by sodium nitrite and dilute hydrochloric acid into  $\alpha$ -oximino- $\beta$ -keto- $\gamma$ -phenylbutyrolactone,  $\text{CHPh} \begin{array}{c} \text{CO}\cdot\text{C:N}\cdot\text{OH} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{CO} \end{array}$ , which crystallises in pale yellow leaflets, m. p. 92—93° (decomp.).

Ethyl phenylacetylglucolyl- $\alpha$ -cyanoacetate (ethyl phenylacetoxycetyl- $\alpha$ -cyanoacetate) is a brownish-yellow oil; the silver salt,



is a white powder.  $\alpha$ -Carbethoxy- $\beta$ -keto- $\gamma$ -phenylbutyrolactam,

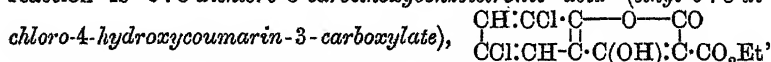


crystallises in small, white, thick leaflets, m. p. 220—223° (decomp.); when treated with dilute aqueous sodium hydroxide, it yields two isomeric acids,  $\text{C}_{11}\text{H}_9\text{O}_4\text{N}$ ; the one crystallises in silvery-white spangles, m. p. 183° (decomp.), and the other is obtained as a fine, soft, white powder, m. p. 178—179°, at which temperature carbon dioxide is eliminated.

W. H. G.

The Benzotetronic Acid [4-Hydroxycoumarin] Group. I. RICHARD ANSCHÜTZ (*Annalen*, 1909, 368, 23—52. Compare this vol., i, 660).—The present communication treats of the condensation reactions of ethyl sodiomalonate, ethyl sodiocyanoacetate, and ethyl sodioacetoacetate with 3:5-dichlorosalicylyl chloride, 3:5-dibromosalicylyl chloride, 3:5-di-iodosalicylyl chloride, 3:5-dinitrosalicylyl chloride, and 1-hydroxy-2-naphthoyl chloride.

[With JEFF HENRY SHORES].—I. Condensation of 3:5-Dichlorosalicylyl Chloride with Ethyl Sodiomalonate.—The product of this reaction is 6:8-dichloro-3-carbethoxybenzotetronic acid (ethyl 6:8-dichloro-4-hydroxycoumarin-3-carboxylate),



crystallising in long, slender, white needles, m. p. 135°; the sodium salt,  $\text{C}_{12}\text{H}_7\text{O}_5\text{Cl}_2\text{Na}$ , forms small, colourless crystals; the ammonium salt forms stellate aggregates of white needles; the silver salt is a white powder, which, when heated with ethyl iodide under pressure at 110°, yields the corresponding ethyl ether,  $\text{C}_{14}\text{H}_{12}\text{O}_5\text{Cl}_2$ , long, slender, white needles, m. p. 148°.

6:8-Dichlorobenzotetronic acid (6:8-dichloro-4-hydroxycoumarin),  $\text{C}_9\text{H}_4\text{O}_3\text{Cl}_2$ , is formed by boiling the parent ester with a solution of potassium hydroxide in 50% alcohol; it crystallises in short, white needles, m. p. 284—285° (decomp.); the silver salt,  $\text{C}_9\text{H}_3\text{O}_3\text{Cl}_2\text{Ag}$ , a white powder, when treated with ethyl iodide, yields the ethyl ether,  $\text{C}_{11}\text{H}_8\text{O}_3\text{Cl}_2$ , long, slender, white needles, m. p. 159°.

[With EMANUEL LÖWENBERG].—II. Condensations with 3:5-Dibromosalicylyl Chloride.—6:8-Dibromo-3-carbethoxybenzotetronic acid (ethyl 6:8-dibromo-4-hydroxycoumarin-3-carboxylate),  $\text{C}_{12}\text{H}_8\text{O}_5\text{Br}_2$ , crystallises in long, slender, white needles, m. p. 153—154°; the sodium,

*ammonium*, and *silver* salts were analysed; the *ethyl ether*,  $C_{14}H_{12}O_5Br_2$ , crystallises in silky, white needles, m. p. 155°. 6 : 8-Dibromo-4-hydroxycoumarin,  $C_9H_4O_3Br_2$ , crystallises in yellow, woolly needles, m. p. 268—269°; the *silver* salt was analysed; the *ethyl ether*,  $C_{11}H_8O_3Br_2$ , forms small, silky, pale yellow needles, m. p. 202°.

6 : 8-Dibromo-3-cyanobenzotetronic acid (6 : 8-dibromo-3-cyano-4-hydroxycoumarin),  $C_{10}H_3O_3NBr_2$ , prepared by the action of 3 : 5-dibromosalicylyl chloride on ethyl sodiocyanoacetate, crystallises in silvery spangles, also in small, slender needles, m. p. 270° (decomp.).

6 : 8-Dibromo-3-acetylbenzotetronic acid (6 : 8-dibromo-4-hydroxy-3-acetylcoumarin),  $C_{11}H_5O_4Br_2$ , prepared by condensing ethyl sodioacetate with 3 : 5-dibromosalicylyl chloride, crystallises in microscopic, pale yellow, silky needles, m. p. 209—210°; the *ammonium* salt was analysed.

[With FRITZ SCHMITZ.]—III. *Condensations with 3 : 5-Diiodosalicylyl Chloride*.—Ethyl 6 : 8-di-iodo-4-hydroxycoumarin-3-carboxylate,  $C_{12}H_8O_5I_2$ , forms white, silky needles, m. p. 235—240°; the *sodium*, *ammonium*, and *silver* salts were analysed; the *ethyl ether*,  $C_{14}H_{12}O_5I_2$ , crystallises in small, colourless needles, m. p. 159°; the *phenylhydrazide*,  $C_6H_5I_2 \begin{smallmatrix} \text{O} \\ \diagup \text{CO} \\ \diagdown \text{CO} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh} \end{smallmatrix}$ , forms small, yellow needles, m. p. 238°.

6 : 8-Di-iodo-3-cyano-4-hydroxycoumarin,  $C_{10}H_3O_3NI_2$ , melts above 285°; the *sodium*, *ammonium*, *copper*, and *silver* salts were analysed; the *ethyl ether*,  $C_{12}H_7O_3NI_2$ , crystallises in small, colourless needles, m. p. 226°. The parent substance, when boiled with dilute hydrochloric acid, yields the corresponding *amide*,  $C_{10}H_5O_4NI_2$ , crystallising in tufts of small, glistening needles, m. p. 256°.

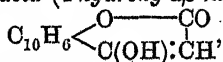
6 : 8-Di-iodo-4-hydroxy-3-acetylcoumarin,  $C_{11}H_5O_4I_2$ , forms pale yellow crystals, m. p. 240—245° (decomp.); the *sodium*, *ammonium*, and *silver* salts were analysed; the *ethyl ether*,  $C_{13}H_{10}O_4I_2$ , has m. p. 125°.

The three condensation products derived from 3 : 5-di-iodosalicylyl chloride do not yield 6 : 8-di-iodo-4-hydroxycoumarin when treated with aqueous potassium hydroxide, but are decomposed, yielding 3 : 5-di-iodosalicylic acid.

[With JULIUS SIEBEN.]—IV. *Action of Ethyl Sodiomalonate on 3 : 5-Dinitrosalicylyl Chloride*.—These two substances do not interact to yield derivatives of benzotetronic acid. The product of the reaction is mainly 3 : 5-dinitrosalicylide (compare Abstr., 1906, i, 505).

[With KARL RUNKEL.]—V. *Condensations with 1-Hydroxy-2-naphthoyl Chloride*.—3-Carbethoxy-(1 : 2)-naphthatetronic acid (ethyl 4-hydroxy- $\alpha\beta$ -naphthapyrone-3-carboxylate),  $C_{10}H_6 \begin{smallmatrix} \text{O} \\ \diagup \text{CO} \\ \diagdown \text{C}(\text{OH}) \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$ , forms yellow needles, m. p. 179°; the *ammonium*, *potassium*, and *silver* salts were analysed; the *ethyl ether*,  $C_{18}H_{16}O_5$ , crystallises in pale yellow needles, m. p. 147°.

(1 : 2)-Naphthatetronic acid (4-hydroxy- $\alpha\beta$ -naphthapyrone),



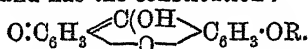
forms greyish-white crystals, m. p. 256—258°.

3-Cyano-(1:2)-naphthatetronic acid (3-cyano-4-hydroxy- $\alpha\beta$ -naphthapyrone),  $C_{14}H_7O_3N$ , crystallises in yellow needles, m. p.  $235^\circ$ ; the potassium and silver salts were analysed; the ethyl ether,  $C_{16}H_{11}O_3N$ , crystallises in leaflets, m. p.  $52^\circ$ . 4-Hydroxy- $\alpha\beta$ -naphthapyrons-3-carboxylamide,  $C_{14}H_9O_4N$ , has m. p.  $182^\circ$ .

4-Hydroxy-3-acetyl- $\alpha\beta$ -naphthapyrone,  $C_{15}H_{10}O_4$ , crystallises in yellow needles, m. p.  $180^\circ$ ; the potassium, copper, and silver salts were analysed; the ethyl ether,  $C_{17}H_{14}O_4$ , forms yellow needles, m. p.  $183^\circ$ .

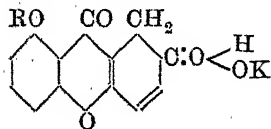
W. H. G.

**Constitution and Colour of Xanthenes and Allied Substances.** JOSEF HERZIG and K. KLIMOSCH (*Monatsh.*, 1909, 30, 527–541. Compare this vol., i, 46).—Some hydroxy-derivatives of the xanthenes, flavones, and flavonols present interesting problems with regard to the relation between colour and constitution. The substances in question are coloured. Hydroxyl groups ortho to the carbonyl are etherified with difficulty, and the resulting ethers are also coloured. Completely etherified derivatives, however, are colourless. The paper deals mainly with exceptions to these generalisations. Euxanthenes forms two types of ethers. One is coloured and insoluble in alkalis, and has the constitution:



The other is colourless and soluble in alkalis, and has hitherto received the constitution:  $OR \cdot C_6H_5 \begin{array}{c} \diagup CO \diagdown \\ \diagdown O \diagup \end{array} C_6H_5 \cdot OH$ . It forms, however, a yellow potassium derivative (which is easily converted into the normal colourless di-alkyl ether), a yellow hydrochloride and stannichloride, and its hydroxyl group is stable to diazomethane, whereas the corresponding group in euxanthone itself is readily methylated by this reagent. The authors suggest, therefore, that the ether has the constitution:  $OR \cdot C_6H_5 \begin{array}{c} CO \cdot C \cdot CH_2 \cdot CO \\ \diagdown O \diagup C \cdot CH \cdot OH \end{array}$ , and that the potassium salt

is an oxonium derivative (annexed constitution) which yields the colourless dialkyl ether owing to transformation into the enol form by loss of water.



Ethers of the first-mentioned type are coloured, and can receive a quinonoid formula. The ethers of morin and of alizarin-yellow (2:3:4-trihydroxybenzophenone) are exceptions, being almost colourless. The first case is explained by the fact that morin itself is almost colourless, and the second by the theory that the colour intensity is repressed by the methoxy-groups.

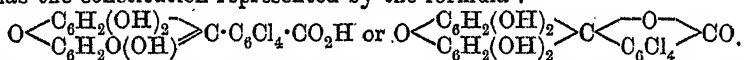
In 2:5-dihydroxybenzophenone, 2:3:4-trihydroxybenzophenone, euxanthone, morin, and alizarin, the hydroxyl group in the ortho (or peri) position to the carbonyl group is not attacked by diazomethane. Only in the case of morin is evidence of such action obtained by the formation of a pentamethoxy-derivative. All other hydroxyl groups are methylated, and the resulting ethers are coloured, with the two

exceptions mentioned above. Fisetin, which does not contain a hydroxyl group thus situated, yields a colourless tetramethyl ether, m. p. 149—150°, with diazomethane.

Some conflicting statements in the literature of 2:3:4-trihydroxybenzophenone receive attention. Graebe and Eichengrün describe a colourless dimethyl ether, and state that further alkylation is impossible. Bartolotti mentions a citron-yellow dimethyl ether, and also a liquid trimethyl ether. The authors find that, in addition to the almost colourless dimethyl ether, m. p. 131°, obtained by the action of diazomethane, 2:3:4-trihydroxybenzophenone yields with methyl sulphate and potassium hydroxide a *trimethyl ether*, m. p. 55°, which crystallises in colourless prisms, and is also obtained by distilling Bartolotti's liquid ether. C. S.

**Tetrachlorogallein and some of its Derivatives.** WILLIAM R. ORNDORFF and T. G. DELBRIDGE (*Amer. Chem. J.*, 1909, 42, 183—271). —Orndorff and Brewer (Abstr., 1900, i, 447) have shown that gallein is the true anhydride of the phthalein of pyrogallol, and reacts tautomerically with formation of two classes of derivatives, namely, coloured compounds of quinonoid structure and colourless compounds of lactoid structure. In the present paper, a résumé is given of recent work on the constitution of the phthaleins, and an account is given of a study of tetrachlorogallein.

The method of preparing tetrachlorogallein described by Graebe (Abstr., 1887, 833) can be improved by the addition of zinc chloride to the mixture of tetrachlorophthalic anhydride and pyrogallol, and in this way a yield amounting to 82% of the theoretical has been obtained. It is shown that tetrachlorogallein is strictly analogous to gallein, and has the constitution represented by the formula :

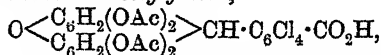


The presence of the carboxyl group is shown by the fact that tetrachlorogallein is capable of forming metallic salts and esters. All these compounds are coloured, and therefore have a quinonoid structure. Anhydrous tetrachlorogallein has only a faint colour, and probably exists in the lactoid form. The presence of the three phenolic hydroxyl groups in the quinonoid modification is demonstrated by the formation of a coloured tetramethyl derivative, which, on hydrolysis, yields a colourless trimethyl ether. Several other colourless derivatives, such as the tetra-acetyl derivative, the tetraphenylcarbamate, and the tetramethyl ether, have also been prepared, and to all of these the lactoid formula is assigned. The existence of these compounds indicates the presence of four phenolic hydroxyl groups in the lactoid modification. It has been found that the trimethyl ether, like tetrachlorogallein itself, is tautomeric; it yields a colourless acetyl derivative and methyl ether, and coloured salts and esters. It is pointed out that this fact does not seem to be in harmony with Baeyer's oscillation theory of the cause of colour in the aniline and aurin dyes (Abstr., 1907, i, 759). Tetrachlorogallein is less basic than gallein, but yields a hydrochloride, as do also its esters.

Tetrachlorogallein has a faint red colour, decomposes at about

320° with evolution of hydrogen chloride, and forms intensely blue solutions with sodium or potassium hydroxide, a bluish-purple solution with ammonia, and reddish-purple solutions with alkali carbonates. On adding acid to a freshly prepared solution in alkali hydroxide, the *hydrate*,  $C_{20}H_8O_7Cl_4 \cdot H_2O$ , is obtained as a red precipitate. The *hydrochloride*, and *sodium*, *potassium*, *lead*, and *barium* salts are described. The *tetra-acetyl* derivative melts at 261° (corr.), and the *tetraphenyl-carbamate* at 182° (uncorr.). *Tetrachlorogallein methyl ester*, m. p. 285—290° (decomp.), forms a dark red, crystalline powder with a slight green lustre, and behaves towards solutions of alkalis in the same manner as tetrachlorogallein itself; its *hydrochloride* is described. The *ethyl ester* melts at 275—280° (decomp.). *Tetrachlorogallein trimethyl ether*, m. p. 253—254° (uncorr.), forms colourless crystals, has fairly strong acid properties, and yields red *sodium* and *ammonium* salts; it is also somewhat basic, and gives a red *hydrochloride*, which decomposes quantitatively at 157° into hydrogen chloride and the colourless trimethyl ether. The *acetyl* derivative of the trimethyl ether, m. p. 252—254°, forms colourless crystals. The *tetramethyl ether* (or, rather, the methyl ester of the trimethyl ether), m. p. 217° (uncorr.), crystallises in prisms, which appear red in transmitted and dark green in reflected light; it yields a red *hydrochloride*. When heated with sodium hydroxide solution, the tetramethyl derivative undergoes hydrolysis, with formation of the colourless trimethyl ether. Evidence has also been obtained of the existence of a colourless tetramethyl ether. *Tetrachlorodiacetylgallein dimethyl ether*, m. p. 225° (uncorr.), forms colourless crystals.

By the reduction of the tetra-acetyl derivative of tetrachlorogallein, a colourless *tetrachlorotetra-acetylgallin*,



m. p. 221—222°, is obtained, which has acid properties; its *silver* salt is white and decomposes at 230—240°. Tetrachlorogallin therefore contains four phenolic hydroxyl groups and one carboxyl group, Orndorff and Brewer's formula for gallin (*loc. cit.*) being thus confirmed.

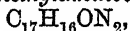
Although tetrachlorogallein and its trimethyl ether contain substituents in both of the ortho-positions to the carboxyl group, they nevertheless yield esters by the ordinary catalytic method of esterification, and are therefore exceptions to Victor Meyer's rule. E. G.

The Basic Power of Dinaphthapyranol is only Manifested in Acid Solution. IX. ROBERT FOSSE (*Bull. Soc. chim.*, 1909, [iv], 5, 827—828).—It has been shown previously (this vol., i, 667) that dinaphthapyranol in acetic acid solution displaces potassium from potassium picrate. It cannot, however, be concluded that the pyranol is a strong base, since its neutral salts (chloride, bromide, etc.), which do not dissolve in cold water, are decomposed by boiling water with liberation of the acid and formation of the pyryl oxide. This hydrolysis explains the absence of basic power of the pyranol in neutral aqueous solution. Dinaphthapyranol\* differs in this respect, not only from the metallic hydroxides, but also from the carbinols of

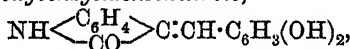
the triphenylmethane series (compare Prud'homme, *Bull. Soc. chim.*, 1895, [iii], 13, 218). E. H.

**Action of Iodine and its Compounds on Adrenaline.** GIUSEPPE COMESSATTI (*Arch. Farmacol. sper. Sci. affini.*, 1909, 8).—In aqueous solutions, iodine compounds exert *in vitro* a distinct anti-adrenaline action, the adrenaline undergoing oxidation to oxy-adrenaline. The action is most active with free iodine, and is more active with potassium iodide than with sodium iodide. When mixed with organic liquids, such as blood-serum, iodine and its compounds no longer exhibit this action. T. H. P.

**isoIndogenides.** ANDRÉ WAHL and P. BAGARD (*Compt. rend.*, 1909, 149, 132—134. Compare this vol., i, 330; Czaplicki, Kostanecki, and Lampe, this vol., i, 236).—A description of new iso-indogenides prepared by the method already described. *Benzylideneoxindole*,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C:CHPh}$ , obtained from benzaldehyde and oxindole, forms sulphur-yellow needles, m. p. 175—176°. *p-Methoxybenzylideneoxindole*,  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$ , crystallises in yellow needles, m. p. 157°. *m-Nitrobenzylideneoxindole*,  $\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}_2$ , occurs in orange leaflets, m. p. 255—257°. *p-Dimethylaminobenzylideneoxindole*,



forms orange-yellow needles, m. p. 194—195°, turning red on exposure to air; it is a basic dye. *o-Hydroxybenzylideneoxindole*,  $\text{C}_{15}\text{H}_{11}\text{O}_3\text{N}$ , forms needles, m. p. 195°; the *meta*-derivative has m. p. about 280°, whilst the *para*-derivative forms small, yellow crystals, m. p. above 300°. 2:4-Dihydroxybenzylideneoxindole,



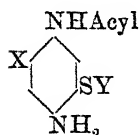
occurs in small, yellow crystals, m. p. above 300°. 3:4-Dihydroxybenzylideneoxindole has m. p. 246°. The hydroxy-derivatives dissolve in aqueous alkalis, giving yellow or orange solutions. W. O. W.

**Preparation of a Sulphur Derivative of Isatin.** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 210343).—By the action of sodium tetrasulphide (30 parts) on indoxyl (30 parts) in alcoholic solution at 80—90°, and subsequent distillation of the solvent, a crystalline paste is obtained, which, when decomposed with dilute hydrochloric acid, gives rise to the compound,  $\text{C}_8\text{H}_5\text{ONS}$ , a brown powder decomposing above 300°. F. M. G. M.

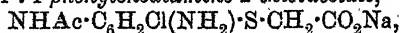
[Preparation of Carbazole Derivatives.] HANS T. BUCHERER and FRANZ SEYDE (D.R.-P. 208960. Compare Japp and Maitland, *Trans.*, 1903, 83, 267).—The condensation of amino- and hydroxy-compounds with phenylhydrazine and sodium hydrogen sulphite is shown to take place in aqueous solution, and therefore at a lower temperature than that indicated by previous workers. With  $\alpha$ - and  $\beta$ -naphthols the chief product is sodium pheno- $\alpha$ - or - $\beta$ -naphthylcarbazole-N-sulphonate,  $\begin{smallmatrix} \text{R} \\ | \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{N} \cdot \text{SO}_3\text{Na}$ , which, on heating with mineral acids,

becomes converted into phenonaphthacarbazole. With  $\alpha$ -naphthol two other compounds are also formed. F. M. G. M.

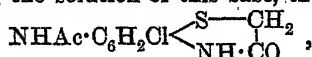
**Preparation of Aromatic Acyl-*p*-diamines.** KALLE & Co. (D.R.-P. 210886).—The *p*-diamines having the annexed general



formula (where X may be chlorine, an alkyl or alkyloxy-group; SY thioalkyl, thioacyl, or chlorine) are prepared as follows: 3:6-Dichloro-4-nitroacetanilide is boiled for four or five hours in 95% alcoholic solution with sodium disulphide prepared by fusing sodium sulphide with the requisite amount of sulphur. On cooling, the mixture sets to a crystalline mass of a *nitrodisulphide* compound, which, after washing with alcohol and water, is sufficiently pure for use in subsequent operations. The nitrodisulphide may be heated in aqueous solution with iron filings and dilute acetic acid, and the reduction mixture treated with sodium hydroxide and chloroacetic acid, when a theoretical yield of *sodium 5-chloro-4-acetyl-1:4-phenylenediamine-2-thiolacetate*,



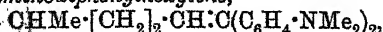
is obtained in a sufficiently pure condition for use in the preparation of dyes. On acidifying the solution of this base, the *anhydride*,



is precipitated in colourless crystals, and, on heating this with dilute sodium hydroxide at 120°, the acetyl group is removed and *sodium 5-chloro-1:4-phenylenediamine-2-thiolacetate* results.

If the reduced nitrodisulphide is treated in alkaline solution with methyl sulphate, the *methyl ether* separates in colourless needles; this compound is almost insoluble in water, but dissolves readily in benzene, alcohol, or acetone. F. M. G. M.

**Some Ethylenic Compounds Containing Nitrogen.** G. BUSIGNIES (*Compt. rend.*, 1909, 149, 348—350. Compare Klages, *Abstr.*, 1902, i, 666).—The action of magnesium methyl iodide on Michler's ketone has been studied by Freund (*Abstr.*, 1906, i, 384); the present communication contains an account of the action of organo-magnesium compounds on other aromatic ketones containing alkylamino-groups. The following new compounds are mentioned: *p*-*Dimethylaminodiphenylethylene*,  $\text{CH}_2 \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , m. p. 47°. *p*-*Dimethylaminodiphenylpropylene*,  $\text{CHMe} \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , m. p. 91°. *pp*-*Tetramethyldiaminodiphenylethylene*,



m. p. 61°. *pp*-*Tetraethyldiaminodiphenylethylene*,  $\text{C}_{22}\text{H}_{30}\text{N}_2$ , m. p. 102°.

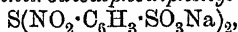
*pp*-*Tetraethyldiaminodiphenylpropylene*,  $\text{C}_{23}\text{H}_{32}\text{N}_2$ , m. p. 56°. When dimethylaminobenzophenone was treated with magnesium benzyl chloride, an intermediate compound was isolated, *dimethylaminodiphenylbenzylcarbinol*,  $\text{CH}_2\text{Ph} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2) \cdot \text{OH}$ , m. p. 131—132°.

The following substances have been obtained by reduction of the corresponding unsaturated compounds: *pp*-*Tetramethyldiaminodiphenylethane*,  $\text{CHMe}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , m. p. 67°. *pp*-*Tetramethyldiamino-*

*diphenyl-phenylethane*,  $\text{CMePh}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , m. p.  $127^\circ$ . *Tetraethyl-diaminodiphenylethane*,  $\text{C}_{22}\text{H}_{32}\text{N}_2$ , m. p.  $45^\circ$ .

The foregoing bases are soluble in organic solvents and in dilute acids. W. O. W.

**Preparation of Sulphonic Derivatives of Thioanilines.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 210564).—When sodium *p*-nitrothiophenyl-*o*-sulphonate (25 parts) is treated in aqueous solution with sodium 2-chloro-5-nitrobenzenesulphonate (26 parts) and boiled during three to four hours, condensation takes place, and the sodium salt of *dinitrodisulphodiphenyl sulphide*,



separates on cooling as a yellow, crystalline powder.

This on reduction with zinc dust in alkaline solution, and subsequent acidification, yields *diaminodisulphodiphenyl sulphide*, a crystalline, grey powder. With sodium *p*-nitrothiophenoxide and sodium 2-chloro-5-nitrobenzenesulphonate, the orange-yellow, crystalline sodium salt of *dinitrosulphodiphenyl sulphide* is obtained. F. M. G. M.

**Basic Properties of the Hydrazones.** ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 100—104).—The basic character of hydrazones is appreciable only in those of aliphatic or hydroaromatic ketones, being very feeble with aromatic hydrazones. This difference is exhibited by the difference in behaviour shown by the two classes of hydrazones with aromatic polynitro-derivatives (compare Abstr., 1906, i, 891, 962; 1907, i, 553).

The author has prepared a number of such additive compounds of hydrazones and aromatic polynitro-derivatives, in order to ascertain if any relation exists between the colours of the compounds and the compositions of the hydrazones from which they are formed. Of the polynitro-derivatives employed, picramide and picryl chloride give the most stable and most intensely coloured compounds, and of the hydrazones, piperonaldehyde phenylhydrazone and phenylmethylhydrazone, which contain an oxymethylene group, give the most stable and intensely coloured compounds.

Another property which is common to the aromatic hydrazones, indoles, carbazoles, and diphenylamine, and should be related to their constitutions, is that of giving with an ethereal solution of tetrachloro-*p*-benzoquinone intense colorations which are sometimes different for substances of similar constitution. The following are the colorations obtained in this way: the phenylhydrazones of benzaldehyde, piperonaldehyde, *m*-nitrobenzaldehyde, and cinnamaldehyde, green; that of anisaldehyde, blue; piperonaldehydephenylmethylhydrazone, green; benzaldehydephenylmethylhydrazone, blue; diphenylamine, dark green; indole, brownish-red; 2-methylindole, violet; 3-methylindole, dirty red; 1-methylindole, blue; pyrrole, wine-red; carbazole, red; tetrahydrocarbazole, violet.

The hydrazones of aliphatic aldehydes and ketones give stable, colourless salts with mineral acids, but the salts formed by the hydrazones of aromatic aldehydes have a more or less intense yellow or brownish-yellow colour. These hydrochlorides, which may be readily

prepared by passing dry hydrogen chloride into the dry ethereal solutions of the hydrazones, remain unchanged when dried out of contact with air, give up their acid more or less easily in a vacuum, and are immediately hydrolysed by water. The hydrazones also give coloured salts with hydrobromic, hydriodic, and sulphuric acids, and with ferric chloride they yield dark green salts. Between the colours of the hydrochlorides and the structures of the corresponding aldehydes there seems to be no close connexion, and when it is considered that colourless benzaldehydephenylhydrazone gives an orange-coloured hydrochloride which forms reddish-brown additive products with trinitrobenzene derivatives, it appears that the intense colour of these additive products is a consequence, partly of the halochromism of the hydrazones, and partly of the nature of the nitro-derivatives themselves. The hydrochlorides of the hydrazones most probably have a quinonoid structure.

T. H. P.

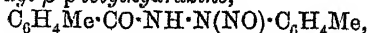
**Action of Water on Nitrosohydrazines.** R. GIOVETTI (*Atti. R. Accad. Sci. Torino*, 1909, 44, 949—956).—It was found by Ponzio (Abstr., 1908, i, 482) that  $\beta$ -nitroso- $\alpha$ -benzoyl- $\beta$ -phenylhydrazine, when boiled with water, is converted into  $\alpha$ -benzoyl- $\beta$ -phenylhydrazine. The author finds that this replacement of the nitroso-group by hydrogen also takes place with the following hydrazine derivatives on boiling them with water:  $\beta$ -nitroso- $\alpha$ -formyl- $\beta$ -phenylhydrazine;  $\beta$ -nitroso- $\alpha$ -formyl- $\beta$ -*p*-tolylhydrazine;  $\beta$ -nitroso- $\alpha$ -*p*-toluoyl- $\beta$ -*p*-tolylhydrazine;  $\beta$ -nitroso- $\alpha$ -anisoyl- $\beta$ -*p*-tolylhydrazine;  $\beta$ -nitroso- $\alpha$ -formyl- $\beta$ -*p*-bromophenylhydrazine;  $\beta$ -nitroso- $\alpha$ -*p*-toluoyl- $\beta$ -*p*-bromophenylhydrazine, and  $\beta$ -nitroso- $\alpha$ -anisoyl- $\beta$ -*p*-bromophenylhydrazine.

$\alpha$ -Formyl- $\beta$ -*p*-tolylhydrazine,  $\text{CHO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared from formic acid (2 mols.) and *p*-tolylhydrazine (1 mol.), crystallises from alcohol in shining, white needles, m. p.  $164^\circ$ .

$\beta$ -Nitroso- $\alpha$ -formyl- $\beta$ -*p*-tolylhydrazine,  $\text{CHO}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_4\text{Me}$ , separates in almost white leaflets, m. p.  $85$ — $86^\circ$  (decomp.), gives Liebermann's reaction, and dissolves in concentrated sulphuric acid, giving a reddish-yellow coloration.

$\alpha$ -*p*-Toluoyl- $\beta$ -*p*-tolylhydrazine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises from alcohol in white needles, m. p.  $177^\circ$ .

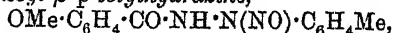
$\beta$ -Nitroso- $\alpha$ -*p*-toluyl- $\beta$ -*p*-tolylhydrazine,



is precipitated from sodium hydroxide solution by addition of acid in yellow plates, m. p.  $110^\circ$  (decomp.), gives Liebermann's reaction, and forms a green solution in concentrated sulphuric acid.

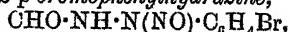
$\alpha$ -Anisoyl- $\beta$ -*p*-tolylhydrazine,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises from alcohol in white needles, m. p.  $158^\circ$ .

$\beta$ -Nitroso- $\alpha$ -anisoyl- $\beta$ -*p*-tolylhydrazine,



separates in yellow laminae, m. p.  $107$ — $109^\circ$  (decomp.), gives Liebermann's reaction, and dissolves in concentrated sulphuric acid, giving a blue solution.

$\beta$ -Nitroso- $\alpha$ -formyl- $\beta$ -*p*-bromophenylhydrazine,



crystallises from a mixture of ether and light petroleum in yellow

plates, m. p. 84—85° (decomp.), gives Liebermann's reaction, and forms a red solution in concentrated sulphuric acid.

*β-Nitroso-α-p-toluoxy-β-p-bromophenylhydrazine*,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_3\text{Br}$ ,  
separates in yellow laminae, m. p. 99—102° (decomp.), gives Liebermann's reaction, and yields a violet coloration in concentrated sulphuric acid.

*β-Nitroso-α-anisoyl-β-p-bromophenylhydrazine*,

$\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{NO})\cdot\text{C}_6\text{H}_3\text{Br}$ ,  
separates in pale yellow laminae, m. p. 100—101° (decomp.), gives Liebermann's reaction, and dissolves in concentrated sulphuric acid, giving a yellowish-red solution.

T. H. P.

**Decomposition of Certain Salts of Silver.** ANGELO ANGELI, VINCENZO CASTELLANA, and R. FERREIRO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 38—46. Compare Angeli and Marchetti, *Abstr.*, 1908, ii, 841).—The silver salt of nitrosophenylhydroxylamine, prepared by double decomposition from the sodium salt, darkens with separation of silver and formation of nitrosobenzene and nitric oxide:  $\text{C}_6\text{H}_5\cdot\text{N}_2\text{O}_2\text{Ag} = \text{Ph}\cdot\text{NO} + \text{NO} + \text{Ag}$ . At the same time, benzenediazonium nitrate is formed, thus:  $\text{Ph}\cdot\text{NO} + 2\text{NO} = \text{Ph}\cdot\text{N}_2\cdot\text{NO}_3$  (compare Bamberger, *Abstr.*, 1897, i, 288), and then decomposes with evolution of nitrogen.

The silver salt of menthonebisnitrosylic acid (compare v. Baeyer, *Abstr.*, 1895, i, 549) decomposes, yielding bisnitrosomenthone, nitric oxide, and silver:  $2\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{N}_2\text{O}_2\text{Ag} = (\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{NO})_2 + 2\text{NO} + 2\text{Ag}$ .

The silver salt of benzenediazoic acid (phenylnitroamine) is, however, stable, and can be crystallised from boiling water, benzenediazoic acid being a stronger acid than nitrosophenylhydroxylamine (compare Hantzsch, *Abstr.*, 1902, i, 209).

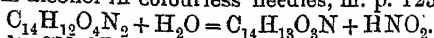
The compound,  $(\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}_2)_2$ , yielded by the decomposition of pernitrosocamphor is probably a derivative of dicamphor, and, like pernitrosocamphor, gives nitrous oxide when treated with concentrated sulphuric acid. It forms a *sodium* salt,  $(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Na}_2$ , and a *diethyl* derivative,  $(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Et}_2$ , which separates from light petroleum in colourless needles, m. p. 140° (decomp.). When treated with carbon dioxide or dilute sulphuric acid, the sodium salt yields a basic compound:  $(\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}_2)_2 = \text{HNO}_2 + \text{C}_{20}\text{H}_{29}\text{O}_2\text{N}_3$ , which separates from benzene in colourless crystals, m. p. 142° (decomp.), and yields a *picrate*,  $\text{C}_{32}\text{H}_{35}\text{O}_{16}\text{N}_9$ , m. p. 147°.

Pernitrosodicamphor also yields a silver salt, which decomposes spontaneously into silver, and a *compound*,  $(\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2)_2$ , which separates from ether in crystals, m. p. 153°, and is formed according to the equations:  $(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Ag}_2 = (\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2)_2 + 2\text{Ag}$  and  $(\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_2)_2 = (\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2)_2 + \text{H}_2$ , the hydrogen being probably readily removed by the silver oxide which is formed.

Silver salts of *isopernitrosufenchone* and *isopernitrosobromocamphor* could not be obtained.

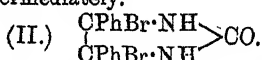
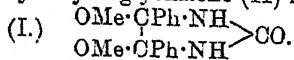
*ω-iso*Nitrotoluene forms a white *silver* salt, which, in presence of ice and ether, decomposes, yielding *α*- and *β*-dinitrotriphenylethanes

(compare Schmidt, Abstr., 1902, i, 21):  $2\text{CHPh}\cdot\text{NO}_2\text{Ag} = 2\text{Ag} + \text{NO}_2\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NO}_2$ , whilst stilbene and silver nitrite are formed at the same time:  $2\text{CHPh}\cdot\text{NO}_2\text{Ag} = \text{CHPh}\cdot\text{CHPh} + 2\text{AgNO}_2$ . The action of sodium ethoxide on  $\beta$ -dinitrodiphenylethane in alcoholic solution yields a small quantity of a product,  $\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}$ , which crystallises from alcohol in colourless needles, m. p.  $125^\circ$ :

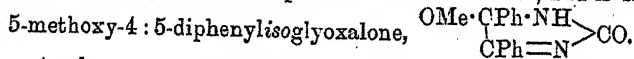


The silver salt,  $\text{CN}\cdot\text{OPh}\cdot\text{NO}_2\text{Ag}$ , is extremely stable. T. H. P.

**Glycols and Glycol-ethers of Glyoxalones and their Isomerism.** HEINRICH BILTZ (*Annalen*, 1909, 338, 156—242).—Whilst investigating the chemical properties of 4:5-diphenylglyoxalone (compare Biltz and Rimpel, Abstr., 1908, i, 573) it was found that the action of small quantities of bromine in methyl alcohol on this compound resulted in the formation of 4:5-dimethoxy-4:5-diphenyldihydroglyoxalone (I), which separated with 1 mol. Me·OH. This compound is probably formed by the action of the alcohol on 4:5-dibromo-4:5-diphenyldihydroglyoxalone (II) formed intermediately.



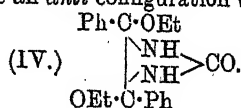
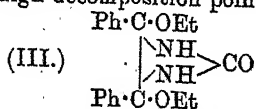
The dimethoxy-compound, with 1Me·OH, when recrystallised from methyl alcohol, yields an isomeride, which decomposes at a higher temperature and loses the alcohol of crystallisation at  $100^\circ$ . The isomeride with the lower temperature of decomposition, when heated at about  $100^\circ$ , loses 2MeOH, but 1MeOH may be removed by shaking the substance with cold ethyl alcohol. The compound formed by the elimination of 2Me·OH from the isomeride with the lower temperature of decomposition is also formed by heating the isomeride with the higher decomposition temperature at about  $200^\circ$ , and is shown to be



Analogous compounds are obtained by replacing the methyl alcohol by ethyl alcohol. Similar compounds have also been prepared by the same method from 4:5-di-*p*-bromophenylglyoxalone, 4:5-diphenyl-1-methylglyoxalone, and 4:5-diphenyl-1-ethylglyoxalone.

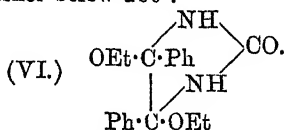
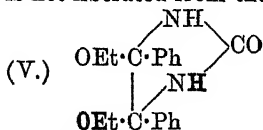
That the alkyloxy-groups occupy positions 4 and 5 is proved (1) by the production of acetylenediureine from the compounds and carbamide; (2) by the formation of benzil and carbamide or their substitution products when the compounds are treated with acids.

The isomerism of these derivatives may be best explained on the assumption that the labile form with the lower temperature of decomposition has a *syn*-configuration (III), whilst the stable modification with the high decomposition point has an *anti*-configuration (IV).



The fact that only the *syn*-compounds give rise to isoglyoxalone derivatives at  $100^\circ$  shows that the imino-hydrogen atoms do not lie in the same plane as the glyoxalone ring; further, the imino-hydrogen

atoms lie on opposite sides of this plane, otherwise the *anti*-ethers would readily part with 1 mol. of alcohol, whilst the *syn*-ethers would give up 2 mols. of alcohol or none at all. The first result of the addition of the two ethoxy-groups to the diphenylglyoxalane is the formation of the *syn*-ether, in which one ethoxy-group must necessarily lie on the same side of the ring as one of the imino-hydrogen atoms: these are printed in heavy type (V). The ease with which 1 mol. of alcohol is eliminated is due to the close proximity of this hydrogen atom and ethoxy-group. The configuration of the *anti*-ether is represented by (VI), in which the imino-hydrogen atoms and the ethoxy-groups are situated on either side of the ring, and, in consequence, alcohol is not liberated from the *anti*-ether below 200°.



The *anti*-forms naturally pass into the *syn*-modifications at the temperatures at which alcohol is eliminated. *anti*-4:5-Diethoxydiphenyldihydroglyoxalane with ethyl alcohol of crystallisation, however, passes into the *syn*-modification when kept in an atmosphere containing a trace of acid.

The alkyloxy-compounds just described may also be prepared directly from the corresponding hydroxy-compounds by treating the alcoholic solutions with a mineral acid. The fact that 4:5-dihydroxy-4:5-di-*p*-bromophenyldihydroglyoxalane when treated with ethyl alcohol and a small quantity of hydrochloric acid below 0° yields the *syn*-ether, shows that the dihydroxy-compound is itself also a *syn*-compound.

The dihydroxy-compounds may be prepared by the following methods: (1) treatment of the glyoxalane with a solution of nitric acid in glacial acetic acid; this method is of general applicability; (2) boiling an alkaline alcoholic solution of benzil or substituted benzil with symmetrical disubstituted carbamides. Carbamide and mono-substituted carbamides yield hydantoin (compare Biltz and Rimpel, Abstr., 1908, i, 462); (3) oxidation of glyoxalones with alkyl groups in positions 1 and 3 by means of potassium permanganate in aqueous acetone; (4) treatment of 4:5-dibromodihydroglyoxalones with water.

The dihydroxy-derivatives are colourless, crystalline substances, which melt and decompose, yielding hydantoin. They are likewise converted by hot acetic anhydride into hydantoin. The same compounds are also formed by boiling with alcohol containing alkali, provided that at least one imino-hydrogen atom is present in the molecule.

The 5-alkyloxyisoglyoxalones are obtained by the following methods: (1) fusion of any ether of the necessary dihydroxydihydroglyoxalane, also by boiling solutions of the ethers in chloroform, benzene, etc.; (2) boiling dihydroxydihydroglyoxalones with alcohol and a small quantity of a mineral acid; (3) action of bromine and ethyl alcohol on the glyoxalane. The last two methods are applicable only when an alkyl group is attached to nitrogen. When treated with alcohol containing acid, they yield dialkyloxy-derivatives, provided the latter are capable of existence.

In conclusion, attention is drawn to many similarities in the chemical properties of uric acid, which contains a glyoxalone ring, and the glyoxalones. The fact that ethers of dihydroxytrimethyluric acid, unlike those of the dihydroxydihydroglyoxalones, do not undergo isomeric change when crystallised from alcohol, is due to the fact that the alkyloxy-groups cannot change places with the CO or NMe group of the pyrimidine ring. It is also evident from this fact that the *anti*-modifications of the dialkyloxydihydroglyoxalones are not produced from the *syn*-isomerides by the hydrogen and nitrogen atoms of one of the imino-groups changing positions.

[With CHAIM RIMPEL.]—4 : 5-Diethoxy-4 : 5-diphenyldihydroglyoxalone,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CPh} \cdot \text{OH} \\ \text{NH} \cdot \text{CPh} \cdot \text{OH} \end{smallmatrix}$ , forms faintly yellow, compact, rhombic crystals, decomposing at 170°. A substance,  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{N}_2$ , was isolated from the product of the oxidation of 4 : 5-diphenylglyoxalone with potassium permanganate; it crystallises in stout, rhombic plates, and decomposes at 215°, yielding diphenylacetylenediureine. *syn*-4 : 5-Diethoxy-4 : 5-diphenyldihydroglyoxalone, as prepared by the methods just described, is obtained with 1Et·OH in microscopic, long, flat, pointed needles; it sinters at about 93°, subsequently becomes solid, and then melts at 185—186°, being the m. p. of 5-ethoxy-4 : 5-diphenylisoglyoxalone. Attempts to remove the 1Et·OH by shaking with methyl alcohol led to displacement of both the ethyl groups by methyl, the compound formed being dimethoxydiphenyldihydroglyoxalone with 1Me·OH. *anti*-4 : 5-Diethoxy-4 : 5-diphenyldihydroglyoxalone,

$\text{C}_{19}\text{H}_{22}\text{O}_3\text{N}_2$ , obtained by crystallising the *syn*-modification from ethyl alcohol, separates with 1Et·OH in four-sided prisms, and decomposes at about 225—230°; the alcohol of crystallisation is eliminated by heating in a vacuum at 100°. The *anti*-compound, free from alcohol of crystallisation, may also be obtained by treating the *syn*-isomeride just described with ether; it decomposes at 224—225°, and crystallises with  $\frac{1}{2}\text{CHCl}_3$  in long prisms. 4 : 5-Dichloro-4 : 5-diphenyldihydroglyoxalone,  $\text{C}_{15}\text{H}_{12}\text{ON}_2\text{Cl}_2$ , prepared by the action of chlorine on a solution of 4 : 5-diphenylglyoxalone in chloroform, crystallises in tufts of thin, pale yellow prisms; it yields the *anti*-ethyl compound just described when crystallised from ethyl alcohol. 5-Ethoxy-4 : 5-diphenylisoglyoxalone,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CPh} \cdot \text{OEt} \\ \text{N} = \text{CPh} \end{smallmatrix}$ , forms compact crystals, m. p. 185°

(190° with short thermometer). When boiled with acetic anhydride it yields the *acetate*,  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2$ , m. p. 172—173°, and when treated with methyl alcohol and one drop of dilute nitric acid it yields dimethoxydiphenyldihydroglyoxalone with 1Me·OH; that is, the ethoxy-group is displaced by a methoxy-group. It is oxidised by chromic acid to dibenzoylcarbamide, and is reduced by zinc dust and acetic acid or by sodium amalgam to diphenylglyoxalone. When its solution in chloroform is treated with hydrogen chloride, it yields 4 : 5-dichloro-4 : 5-diphenyldihydroglyoxalone, and with chlorine, it yields 3 : 4-dichloro-5-ethoxy-4 : 5-diphenylisoglyoxalone,  $\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_2\text{Cl}_2$ , obtained in small, white crystals.

The following compounds, unless otherwise stated, are obtained by methods similar to those employed in the preparation of the analogous compounds just described.

*syn-4:5-Dimethoxy-4:5-diphenyldihydroglyoxalone*,  $C_{17}H_{18}O_3N_2$ , crystallises in small, flat prisms, decomposing at about  $115^\circ$ ; the compound with  $1Me\cdot OH$  forms rounded, mussel-shaped crystals, decomposing at about  $118^\circ$ . The *anti-isomeride* forms long needles, m. p.  $217^\circ$  (decomp.); the compound with  $1Me\cdot OH$  crystallises in well-defined octahedra and decomposes at about  $214-215^\circ$ . *5-Methoxy-4:5-diphenylisoglyoxalone*,  $C_{16}H_{14}O_3N_2$ , forms small, compact crystals with rhombic facets, m. p.  $179-180^\circ$ ; the *acetate*,  $C_{18}H_{16}O_3N_2$ , crystallises in large prisms, m. p.  $180^\circ$ .

*4:5-Dihydroxy-4:5-diphenyl-1-methyldihydroglyoxalone*,  $C_{16}H_{16}O_3N_2$ , crystallises in nodular aggregates of prisms, m. p.  $150^\circ$  (decomp.); when heated alone, or with an alcoholic solution of alkali, it yields *5:5-diphenyl-3-methylhydantoin*; the *syn-dimethyl ether*,  $C_{18}H_{20}O_3N_2$ , forms colourless crystals and decomposes at  $110^\circ$ ; the *anti-isomeride* crystallises in aggregates of glistening, long prisms and decomposes at  $188^\circ$ . *5-Methoxy-4:5-diphenyl-1-methylisoglyoxalone*,  $C_{17}H_{16}O_2N_2$ , forms white crystals, m. p.  $152^\circ$ . Attempts to prepare the diethoxy-derivative of the glyoxalone were unsuccessful; in each case *5-ethoxy-4:5-diphenyl-1-methylisoglyoxalone*,  $C_{18}H_{18}O_2N_2$ , was formed; it crystallises in rosettes of small crystals, m. p.  $155^\circ$ .

*4:5-Diphenyl-1:3-dimethylglyoxalone* is best prepared by the action of methyl sulphate on *4:5-diphenyl-1-methylglyoxalone*; the dihydroxy-derivative has already been described (compare Abstr., 1908, i, 218). It does not yield ethers when treated by the methods described above. *4:5-Dibromo-4:5-diphenyl-1:3-dimethyldihydroglyoxalone*,  $C_{17}H_{18}ON_2Br_2$ , crystallises in red, rhombic plates, sinters at  $120^\circ$ , m. p. about  $140^\circ$  (decomp.).

*syn-4:5-Diethoxy-4:5-di-p-bromophenyldihydroglyoxalone*,  $C_{19}H_{20}O_3N_2Br_2$ , forms white crystals and decomposes at  $125-130^\circ$ ; the compound with  $1Et\cdot OH$  crystallises in four-cornered plates and decomposes at  $121-122^\circ$ ; the *anti-isomeride* crystallises in prisms, m. p.  $266-268^\circ$  (decomp.). *5-Ethoxy-4:5-di-p-bromophenylisoglyoxalone* was obtained as a vitreous mass which could not be crystallised.

[With P. KREBS.]—*4:5-Dihydroxy-4:5-di-p-methoxyphenyl-1:3-dimethyldihydroglyoxalone*,  $C_{19}H_{22}O_5N_2$ , crystallises in prisms with rhombic facets, m. p.  $193^\circ$  (decomp.). *5:5-Di-p-methoxyphenyl-1:3-dimethylhydantoin*,  $C_{19}H_{20}O_4N_2$ , forms small, slender, colourless needles, m. p.  $114^\circ$ .

[With TH. KOSEGARTEN.]—*Tetraphenyglyoxalone*,  $C_{27}H_{20}ON_2$ , prepared by boiling a solution of benzoïn and diphenylhydantoin in glacial acetic acid, crystallises in colourless, small leaflets, m. p.  $207^\circ$ . When treated with chromic acid, it yields *s-dibenzoyldiphenylcarbamide*,  $CO(NPhBz)_2$ , crystallising in tufts of colourless, hexagonal leaflets, m. p.  $200^\circ$  (decomp.). The *dihydroxy-derivative*,  $C_{27}H_{22}O_3N_2$ , forms large crystals with rhombic and hexagonal facets, sinters at about  $160^\circ$ , and decomposes at about  $178^\circ$ . All attempts to prepare ethers of it were unsuccessful. *1:3:5:5-Tetraphenylhydantoin*,  $C_{27}H_{20}O_2N_2$ , crys-

tallises in long, rhombic leaflets, m. p. 186°. Tetraphenylglyoxalane does not condense with diphenylcarbamide when heated with glacial acetic acid and bromine; the only compound formed is *s*-di-*p*-bromophenylcarbamide, which commences to darken at 300°, sinters at 320°, and decomposes at about 330°. The m. p. recorded by Portner (Abstr., 1899, i, 136) is incorrect.

4 : 5-Diphenyl-1-ethylglyoxalane,  $C_{17}H_{16}ON_2$ , prepared from benzoin and ethylcarbamide, or from diphenylglyoxalane and ethyl sulphate, forms colourless crystals, m. p. 260°; the acetate,  $C_{19}H_{18}O_3N_2$ , crystallises in needles, m. p. 122—123°. The dihydroxy-derivative,  $C_{17}H_{16}O_3N_2$ , forms glistening, transparent crystals, m. p. 191—192° (decomp.); at this temperature it passes into 5 : 5-diphenyl-3-ethylhydantoin (compare Abstr., 1908, i, 462); the syn-dimethoxy-derivative,  $C_{19}H_{20}O_3N_2$ , forms small crystals, m. p. about 81° (slight decomp.); the anti-isomeride (?) has m. p. 185° (slight decomp.). Attempts to prepare the corresponding diethoxy-derivatives resulted in the formation of 5-ethoxy-4 : 5-diphenyl-1-ethylisoglyoxalane,  $C_{19}H_{20}O_3N_2$ , colourless prisms, m. p. 104°. The latter substance when treated with methyl alcohol and a trace of hydrochloric acid yields 4 : 5-dihydroxy-4 : 5-diphenyl-1-ethyldihydroglyoxalane. This, when treated with an alcoholic solution of carbamide in the presence of hydrochloric acid, yields 4 : 5-diphenyl-1-methyl-acetylenediureine,  $CO \begin{matrix} \text{NEt} \cdot \text{CPh} \cdot \text{NH} \\ \text{NH} \cdot \text{CPh} \cdot \text{NH} \end{matrix} CO$ , which crystallises in colourless, felted needles, m. p. 284—285° (decomp.); the diacetate,  $C_{22}H_{22}O_4N_4$ , forms long, slender prisms, m. p. 220° (decomp.).

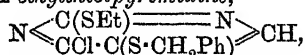
4 : 5-Diphenyl-1 : 3-diethylglyoxalane,  $C_{19}H_{20}ON_2$ , forms small, colourless crystals, m. p. 138°. When oxidised with chromic acid, it yields dibenzoyldiethylcarbamide,  $CO(NEtBz)_2$ , hexagonal leaflets, m. p. 151—152°. The dihydroxy-derivative,  $C_{19}H_{22}O_3N_2$ , forms colourless, glistening crystals, m. p. 157·5° (decomp.), and when fused yields 5 : 5-diphenyl-1 : 3-diethylhydantoin,  $C_{19}H_{20}O_2N_2$ , long, slender prisms, m. p. 110°. The glyoxalane does not yield dialkylglyoxy-derivatives when treated with alcohol and bromine.

W. H. G.

**Pyrimidines. XLV. Sulphur Derivatives of 5-Hydroxyuracil: Preparation of 5-Benzylthioluracil and 5-Benzylthiocytosine.** TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1909, 42, 271—287).—It has been shown by several authors that the hydrogen atoms of the methylene group of cyclic compounds containing the  $\cdot S \cdot CH_2 \cdot CO \cdot$  complex, such as rhodanic acids and  $\psi$ -thiohydantoins, react with aldehydes in presence of alkali with formation of unsaturated condensation products. It has also been found that the methylene group of aryl- $\psi$ -thiohydantoins is capable of condensing with ethyl oxalate in presence of sodium ethoxide, but it does not appear that an attempt has ever been made to condense ethyl oxalate or ethyl formate with an acyclic compound containing the complex  $\cdot S \cdot CH_2 \cdot CO \cdot$ . Experiments have therefore been made in order to ascertain if ethyl formate would condense with a thio-ether of ethyl thioglycollate,  $SH \cdot CH_2 \cdot CO_2Et$ , with production of an  $\alpha$ -thiol derivative of  $\beta$ -hydroxyacrylic acid.

When the sodium derivative of ethyl benzylthioglycollate (Gabriel,

Abstr., 1880, 34) is treated with ethyl formate in presence of sodium, ethyl  $\beta$ -hydroxy- $\alpha$ -benzylthiolacrylate,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{Et}$ , m. p. 57—58°, is obtained, which gives a bright red colour with ferric chloride. The sodium derivative of this compound condenses smoothly with ethyl- $\psi$ -thiocarbamide, yielding 5-benzylthiol-2-ethylthiol-6-pyrimidone,  $\text{NH}\langle\begin{smallmatrix} \text{C}(\text{SEt})=\text{N} \\ \text{CO}\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 155—156°, which forms tabular crystals, and is converted by strong hydrochloric acid into 5-benzylthioluracil,  $\text{NH}\langle\begin{smallmatrix} \text{CO}=\text{NH} \\ \text{CO}\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 290°, which crystallises in rhombic plates or tablets. 5-Benzylthiol-2-ethylthiol-6-pyrimidone reacts with phosphoryl chloride with formation of 6-chloro-5-benzylthiol-2-ethylthiolpyrimidine,



m. p. 47—48°, which crystallises in prisms and is converted by alcoholic ammonia into 6-amino-5-benzylthiol-2-ethylthiolpyrimidine, m. p. 68—69°, which forms groups of needles. When this amino-derivative is boiled with concentrated hydrochloric acid, ethyl mercaptan is evolved and 5-benzylthiolcytosine,  $\text{N}\langle\begin{smallmatrix} \text{CO}=\text{NH} \\ \text{C}(\text{NH}_2)\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 240—241°, is produced, which crystallises in plates. When 5-benzylthiol-2-ethylthiol-6-pyrimidone is heated in a current of dry hydrogen chloride at 160—170°, ethyl chloride is produced, together with 2-thio-5-benzylthiol-6-pyrimidone,  $\text{NH}\langle\begin{smallmatrix} \text{CS}=\text{NH} \\ \text{CO}\cdot\text{C}(\text{S}\cdot\text{CH}_2\text{Ph}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 195—196°.

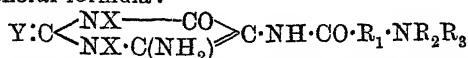
6-Chloro-5-ethoxy-2-methylthiolpyrimidine,  $\text{N}\langle\begin{smallmatrix} \text{C}(\text{SMe})=\text{N} \\ \text{CCl}\cdot\text{C}(\text{OEt}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 75°, obtained by the action of phosphoryl chloride on 5-ethoxy-2-methylthiol-6-pyrimidone (Johnson and McCollum, Abstr., 1906, i, 705), crystallises in slender prisms, and, when heated with alcoholic potassium hydrosulphide, is converted into 6-thio-5-ethoxy-2-methylthiolpyrimidine,  $\text{NH}\langle\begin{smallmatrix} \text{C}(\text{SEt})=\text{N} \\ \text{CS}\cdot\text{C}(\text{OEt}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 190°, which forms light yellow prisms.

2:6-Dichloro-5-ethoxypyrimidine,  $\text{N}\langle\begin{smallmatrix} \text{CCl}=\text{N} \\ \text{CCl}\cdot\text{C}(\text{OEt}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 41—42°, obtained by the action of phosphoryl chloride on 5-ethoxyuracil (Johnson and McCollum, *loc. cit.*), forms prisms or needles, and is converted by potassium hydrosulphide into 2:6-dithio-5-ethoxypyrimidine (dithio-5-ethoxyuracil),  $\text{NH}\langle\begin{smallmatrix} \text{CS}=\text{NH} \\ \text{CS}\cdot\text{C}(\text{OEt}) \end{smallmatrix}\rangle\text{CH}$ , which crystallises in needles and decomposes above 255°.

The sodium derivative of ethyl  $\beta$ -hydroxy- $\alpha$ -phenoxyacrylate condenses with thiocarbimide with formation of 2-thio-5-phenoxy-6-pyrimidone,  $\text{NH}\langle\begin{smallmatrix} \text{CS}=\text{NH} \\ \text{CO}\cdot\text{C}(\text{OPh}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 253—254°, which forms clusters of prisms, and is converted by concentrated hydrochloric or hydrobromic acid into 5-phenoxyuracil,  $\text{NH}\langle\begin{smallmatrix} \text{CO}=\text{NH} \\ \text{CO}\cdot\text{C}(\text{OPh}) \end{smallmatrix}\rangle\text{CH}$ , m. p. 290° (decomp.), which crystallises in needles.

E. G.

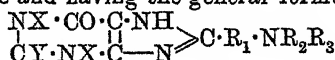
**Preparation of Pyrimidine Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 209729).—Pyrimidine derivatives having the general formula:



(where X is hydrogen or an alkyl group; Y acidic, sulphur, imino-, or cyanimino-residues;  $R_1$  an alkyl group, and  $R_2$  and  $R_3$  hydrogen, alkyl, or aryl residues) are intermediate products for the preparation of therapeutically active purine derivatives (following abstract). 4-Amino-2:6-diketo-5-chloroacetyl-amino-1:3-dimethylpyrimidine (200 parts) is heated in an autoclave with 30% ammonium hydroxide (1000 parts) to 50° during ten hours. The excess of water and ammonia are evaporated, and the residue treated with 90% alcohol (500 parts), when 4-amino-5-aminoacetyl-amino-2:6-diketo-1:3-dimethylpyrimidine, white powder, m. p. 220°, remains undissolved, being only sparingly soluble in this medium, ether, or benzene, but readily so in water.

If piperidine replaces the ammonium hydroxide in this reaction, the piperidyl derivative, prismatic crystals, m. p. 98°, is obtained; it is readily soluble in hot water, alcohol, and alkali hydroxides, but only slightly soluble in cold water. 4-Amino-5(β)-chloro-α-hydroxy-propionyl-amino-2:6-diketo-1:3-dimethylpyrimidine, when condensed with dimethylamine, yields the 5(β)-dimethylaminolactyl-amino-pyrimidine derivative, m. p. 228°, easily soluble in water and alkali hydroxides, but insoluble in alcohol or ether. 4-Amino-5-phenyl-aminoacetyl-amino-2:6-diketo-3-methylpyrimidine, m. p. 275°, soluble in the ordinary organic media, but insoluble in hot water, is obtained from 4-amino-5-chloroacetyl-amino-2:6-diketo-3-methylpyrimidine (m. p. 225°) on warming with aniline. F. M. G. M.

**Preparation of Basic Purine Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 209728).—Basic purine derivatives of therapeutic value and having the general formula:

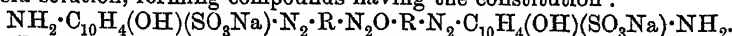


(where X is hydrogen or an alkyl group; Y acyl, sulphur, imino-, or cyanimino-groups;  $R_1$  an alkyl group;  $R_2$  and  $R_3$  hydrogen, alkyl, or aryl residues) are produced when aminoaminoacylpyrimidine derivatives (compare preceding abstract) are treated with alkaline condensing agents, and the preparation of the following is described in the patent. 8-Aminomethyl-1:3-dimethylxanthine, m. p. 252° (decomp.), from 4-amino-5-aminoacetyl-amino-2:6-diketo-1:3-dimethylpyrimidine and sodium hydroxide (30%), is soluble in alkalis, but only sparingly soluble in alcohol, ether, or chloroform; with acids it forms soluble, stable, neutral salts. 1:3-Dimethyl-8-piperidylmethylxanthine, colourless needles, m. p. 203°, is obtained from 4-amino-2:6-diketo-1:3-dimethyl-5-piperidylacetylaminopyrimidine and sodium ethoxide.

Other reagents, such as barium hydroxide and magnesia, can be used for these condensations. F. M. G. M.

[Reduction of Nitrodiazo-compounds to Azoxy-derivatives.] LEOPOLD CASSELLA & Co. (D.R.-P. 211029).—p-Nitrodiazo-compounds

are reduced in alkaline solution, yielding the azoxydiamines; these are diazotised and coupled with 6-amino- $\alpha$ -naphthol-3-sulphonic acid in acid solution, forming compounds having the constitution:

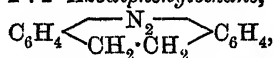


These substances dye cotton in yellow to violet-red shades, which are fast to light.

F. M. G. M.

**Attempts at Benzidine Formation in the Diphenyl, Diphenylmethane, and Diphenylethane Series.** HENRI DUVAL (*Compt. rend.*, 1909, 149, 401—402. Compare Abstr., 1905, i, 651; 1906, i, 314).—The author summarises his previous work on this subject. Reduction of 2:2'-dinitro-4:4'-tetramethylidiaminodiphenylmethane by zinc dust in presence of pyridine and hydrochloric acid, followed by oxidation in a current of air, the operation being repeated using zinc dust and sodium hydroxide as the reducing agent, leads to the formation of 4:4'-tetramethylidiamino-2:2'-azodiphenylmethane,

$\text{NMe}_2 \cdot \text{C}_6\text{H}_3 \langle \text{CH}_2 \rangle \text{C}_6\text{H}_3 \cdot \text{NMe}_2$ , red spangles, m. p. 213°. *Azoxydiphenylmethane-4:4'-dicarboxylic acid*, obtained by the reduction of ethyl dinitrodiphenylmethane-4:4'-dicarboxylate with zinc dust and ammonium chloride, followed by oxidation, forms an *ethyl ester*, which on reduction by zinc dust and acetic acid, and subsequent treatment with mercuric oxide, furnishes *ethyl azodiphenylmethane-4:4'-dicarboxylate*,  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_3 \langle \text{CH}_2 \rangle \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{Et}$ , crystallising in yellow spangles, m. p. 233°. 2:2'-Azodiphenylethane,



yellow needles, m. p. 112.5°, is obtained by boiling 2:2'-dinitrodiphenylethane with barium hydroxide and zinc dust in dilute alcoholic solution and then oxidising the product with mercuric oxide.

W. O. W.

**Relations between  $\alpha$ -Benzaldehydephenylhydrazone and other Nitrogen Compounds.** ROBERTO CIUSA and UGO PESTALOZZA (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 90—93).—The authors have carried out experiments to ascertain whether there exists any analogy in chemical behaviour between  $\alpha$ -benzaldehydephenylhydrazone and diazoaminobenzene (m. p. 96°), which may be regarded as the phenylhydrazone of nitrosobenzene.

The action of picric acid or picryl chloride on  $\alpha$ -benzaldehydephenylhydrazone in benzene solution gives, in each case, the corresponding intensely brown additive compound. With diazoaminobenzene (1 mol.), picric acid (1 mol.) in 96% alcoholic solution yields benzene-diazonium picrate, which may conveniently be prepared in this way; picric acid evidently acts on diazoaminobenzene in the same manner as does hydrochloric acid:  $\text{N}_2\text{Ph} \cdot \text{NHPh} + 2\text{HCl} = \text{Ph} \cdot \text{N}_2\text{Cl} + \text{Ph} \cdot \text{NH}_2 \cdot \text{HCl}$ .

The action of amyl nitrate on diazoaminobenzene, studied with the view of obtaining oxidation products containing a chain of six nitrogen atoms, is very complex, the only identifiable product obtained being benzenediazonium nitrate,

The action of mercuric oxide on diazoaminobenzene in chloroform solution yields only a mercury salt of diazoaminobenzene,  
 $(N_2Ph \cdot NPh)_2Hg$ ,

m. p. 232°.

The differences in the behaviour of diazoaminobenzene and benzaldehydephenylhydrazone towards amyl nitrate and mercuric oxide (compare Minunni and Rap, Abstr., 1897, i, 40; von Pechmann, Abstr., 1893, i, 461) are explained by the acid character of the former compound and the feebly basic nature of the latter. T. H. P.

**Nomenclature of Lipoids.** OTTO ROSENHEIM (*Bio-Chem. J.*, 1909, 4, 331—336).—The author proposes to omit all names given to substances insufficiently characterised, or which are mixtures, and to adopt in the case of different names for the same substances, those proposed by the original discoverer. The following names should therefore be discarded: *cérébrote*, *cerebric acid*, *protagon*, *cerebrin*, *pseudocerebrin*, *cerebron*, *homo-cerebrin*, and *myelin*. The names retained would be: *cholesterin* and *phytosterin* in the group free from nitrogen and phosphorus; *phrenosin* and *kerasin* in the group of cerebro-galactosides; and *lecithin*, *kephalin*, *vesalthin*, *sphingomyelin*, *neottin*, and *cuorin* in the phosphatide group. According to Thudichum's original classification, the phosphatides are arranged according to their N:P ratio. The name *cholesterin* is preferred to *cholesterol*, as it has the advantage of long and international usage; the new termination represents only one characteristic of the substance, namely, its alcoholic nature.

W. D. H.

**Action of Methyl Iodide on Casein.** ZDENKO H. SKRAUP and E. KRAUSE (*Monatsh.*, 1909, 30, 447—465).—The reaction was studied with the object of ascertaining whether or not the protein molecule contains free amino-groups. The authors were able to obtain a 40% yield of methyl derivative containing iodine, which latter element they consider to be present, to some extent, in the quaternary form; on hydrolysis this substance yielded no tyrosine or lysine, and only traces of histidine and arginine, but considerable quantities of glutamic acid and leucine, and also phenylalanine; the substance does not give Millon's reaction, but gives the biuret and Molisch reactions just like ordinary casein; the Liebermann reaction, however, is rather less marked, while the glyoxylic acid reaction is more intense. From these facts the conclusion is drawn that, on methylation, the glutamic acid, leucine, and possibly phenylalanine residues remain intact, whereas the tyrosine complex and the hexone bases are destroyed.

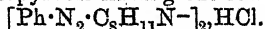
Purified casein was found to contain a small, yet constant, quantity of methyl, both in the form of  $\cdot OMe$  and  $\cdot NMe$ , and from the figures obtained the minimum molecular weight of casein was calculated to be 3500.

*Methyliodocasein*, when finely powdered, is a faintly yellow-coloured substance, which has a slightly acid reaction to litmus; when freshly prepared it is only partly soluble in water, but, after keeping for some time in closed vessels, it is completely soluble; concentrated aqueous solutions are practically clear, and are not rendered turbid by the

addition of ammonia, but sulphuric acid produces a marked precipitate. A heavy precipitate is also produced on half saturation with ammonium sulphate. P. H.

**Hæmatin.** WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1909, 61, 164—176).—Mostly polemical against Piloty (this vol., i, 539). While recognising the importance of Piloty's discovery of hæmopyrrole-carboxylic acid, the author does not agree with the suggestion that each hæmatin molecule gives only one molecule of this acid, but thinks that the complex yielding it occurs twice. If, as Piloty believes, hæmopyrrole is formed by the reduction of an independent complex,  $\text{CR}=\text{C} \begin{smallmatrix} \diagup \\ \text{NH} \\ \diagdown \end{smallmatrix} \text{CR}_1:\text{C}$ , the imide of a  $\beta\beta'$ -disubstituted maleic acid should be formed on oxidation, but no such compound can be detected. The oxidation of hæmatoporphyrin by chromic acid in sulphuric acid solution (instead of in glacial acetic acid) results in the formation of two molecules of hæmatic acid, one of acetic acid, and four of carbon dioxide. G. B.

**Blood-pigment. X.** LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1909, 61, 276—278).—The product obtained by the action of benzenediazonium chloride on hæmopyrrole, which forms ruby-red, rhombic crystals, m. p. 268° (compare Abstr., 1908, i, 843), is shown to be the hydrochloride of a substance resulting from the coupling of two molecules of benzeneazohæmopyrrole having the formula



An analogous product,  $[\text{Ph} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_7\text{N}]_2 \cdot \text{HCl}$ , has been prepared by the action of benzenediazonium chloride on 2:4-dimethylpyrrole.

Comparison of the absorption spectra of the bisazo-derivatives of pyrrole with that of the azo-derivative obtained from hæmopyrrole, the hydrochloride of which has m. p. 233° (*loc. cit.*), points to the probability that hæmopyrrole is a dimethylethylpyrrole. W. H. G.

**Hippomelanin. II.** OTTO RIESSER and PETER RONA (*Zeitsch. physiol. Chem.*, 1909, 61, 12—15).—The base described previously (compare Abstr., 1908, i, 1028), resulting from the action of a 3% solution of hydrogen peroxide containing a small quantity of hydrochloric acid on hippomelanin, is shown to be guanidine.

A second base, which is precipitated by phosphotungstic acid, was also isolated. The *picrate* is deposited as an oil sparingly soluble in alcohol; the *hydrochloride* crystallises in long, indistinct needles; a *platinichloride* insoluble in alcohol could not be obtained. W. H. G.

**Constitution of Gelatin.** ZDENKO H. SKRAUP and A. VON BIEHLER (*Monatsh.*, 1909, 30, 467—479).—The fact that the combined weight of the products of hydrolysis of most proteins falls considerably short of the weight of the substance hydrolysed induced the authors to repeat the hydrolysis of gelatin with the object of ascertaining whether this discrepancy was due to the imperfection of Fischer's ester method or whether any products were formed which had escaped

detection. By repeated and exhaustive esterification of the products of hydrolysis of gelatin, the authors have been able to account for 86% of the substance, but have not been able to discover any new products.

P. H.

#### Formation of Oxalic Acid from Gelatinous Substances.

W. S. SADIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 641—651; *Biochem. Zeitsch.*, 1909, 21, 35—45).—Oxidation of thioglutan (Abstr., 1907, i, 740) with concentrated nitric acid results in the formation of oxalic acid, the amount of which varies with the conditions employed. Glutin also gives oxalic acid when oxidised by concentrated nitric acid, but only when calcium salts are present; with collagen, the presence of calcium salts is unnecessary.

When heated with potassium hydroxide solution at 240° (under which conditions little or no decomposition of oxalic acid occurs), glutin gives oxalic acid, the greatest yield obtained being 146.9%, corresponding with 39.17% of the carbon of the glutin; traces of carbon are lost in the form of volatile products, such as pyrrole, indole, etc. The yield of oxalic acid under these conditions is not increased by energetic hydration of the glutin by means of concentrated hydrochloric acid. Similar formation of oxalic acid from thioglutan and collagen is observed, the rate of formation being in both cases less than with glutin.

T. H. F.

**Mono-amino-acids in the Muscular Substance of Egyptian Mummies.** I. EMIL ABDERHALDEN and CARL BRAHM (*Zeitsch. physiol. Chem.*, 1909, 61, 419—420).—The following amino-acids were identified, 50 grams of the neck muscle serving as the material worked with: glycine, alanine, leucine, phenylalanine, and glutamic acid.

W. D. H.

**Comparative Investigation of the Composition and Structure of Various Kinds of Silks.** III. The Mono-amino-acids of Shantung Tussore Silk. EMIL ABDERHALDEN and CARL BRAHM. IV. Mono-amino-acids from Bengal Silk. EMIL ABDERHALDEN and JAMES SINGTON (*Zeitsch. physiol. Chem.*, 1909, 61, 256—258, 259—260. Compare this vol., i, 343).—The following table gives the main results obtained; the figures are percentages.

	Shantung Tussore silk.	Bengal silk.
Glycine.....	14.5	30.5
Alanine.....	22.0	20.0
Serine .....	1.8	1.75
Leucine.....	1.0	1.2
Aspartic acid .....	1.0	0.8
Glutamic acid.....	1.75	traces
Phenylalanine.....	1.0	1.4
Tyrosine .....	9.7	10.0
Proline.....	2.5	1.0

W. D. H.

Comparative Hydrolysis of Silk by Boiling, Fuming Hydrochloric Acid, 25 per cent. Sulphuric Acid, 20 per cent. Aqueous Sodium Hydroxide, and Hot Saturated Baryta Solution. EMIL ABDERHALDEN, F. MEDIGRECEANU, and LUDWIG PINCUSOHN (*Zeitsch. physiol. Chem.*, 1909, 61, 205—209).—Within narrow limits the same quantities of amino-acids were obtained from silk whether the hydrolysis is accomplished by acids or by alkalis.

W. D. H.

Deaminoproteins. S. J. LEVITES (*Biochem. Zeitsch.*, 1909, 20, 224—230).—Skraup's observation (compare Abstr., 1906, i, 913) is confirmed that in deaminoproteins the amount of diamino-nitrogen is diminished, chiefly owing to the disappearance of lysine, which is apparently converted into a monoamino- or aminohydroxy-acid.

G. B.

Action of Ferments on Stachyose. J. VINTILESCO (*J. Pharm. Chin.*, 1909, [vi], 30, 167—173).—Tanret has shown that the hydrolysis of stachyose (manneotetrose) can be effected in two stages by the use of acetic acid followed by sulphuric acid (Abstr., 1902, i, 661; 1902, i, 606); the present communication shows that the same result may be brought about by the successive action of invertin and the emulsin of almonds. The latter contains a specific enzyme which brings about fission of the manninotriose formed in the first stage. This ferment, for which the name "*manninotriase*" is suggested, has been isolated from top fermentation yeast cultivated in a solution containing stachyose (extract of *Stachys tuberosa*). The hydrolytic action on stachyose is slow, and depends on the amount of enzyme present; acetic acid has an accelerating influence. It is without action on salicin and lactose, but partly hydrolyses amygdalin with formation of a reducing sugar, but not of hydrogen cyanide.

W. O. W.

The Enzymes of Gum-acacia and certain other Gums. FRIEDRICH REINITZER (*Zeitsch. physiol. Chem.*, 1909, 61, 352—394).—The author has repeated and confirmed his earlier observations (Abstr., 1890, 998), and combats many of the statements of Wiesner (*Sitz. Wiener Akad.*, 1885, 92, 40) and Grafe (*Wiesner-Festschrift, Wien*, 1908, 253). It is definitely established, in opposition to the statements of these authors, that gum-acacia, cherry gum, and gum-tragacanth contain an enzyme (gum-amylase), present in widely varying quantities, capable of converting starch into dextrin and maltose. Experiments are cited which tend to show that these gums also contain another enzyme, capable of bringing about the dissolution of starch, but unable to convert it into maltose. These enzymes may be separated more or less completely by filtering the solution of the gum through a porcelain filter.

All the gums investigated were also found to contain varying amounts of oxydases, probably identical with laccase (compare Bertrand, Abstr., 1895, i, 368) and peroxydases.

The enzymes present in gum-acacia are incapable of converting

insoluble gums into soluble gums or into sugar; it is to be inferred, therefore, that, contrary to the statements of Wiesner and Grafe, they would not have any action on celluloses or hemicelluloses.

W. H. G.

**Invertin (Invertase) of Yeast. II.** ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1909, 61, 124—138).—Invertase does not contain carbohydrates; the yeast gum generally accompanying it is an impurity, and by extraction with cold chloroform water under certain conditions dilute invertase solutions may be obtained which are carbohydrate free. In contradistinction to what is generally supposed, press yeast gives off appreciable quantities of invertase to pure water. Invertase appears to be particularly resistant to putrefaction.

G. B.

**Purification of Peroxydase.** N. T. DELEANO (*Biochem. Zeitsch.*, 1909, 19, 266—269).—Peroxydase is abundant during the germination of the seeds of *Ricinus communis*. In the extracts it is mixed with other substances, especially protein. It can be separated from the protein by precipitating the latter with Kahlbaum's colloidal iron solution (lig. ferri oxyd. dialys. colloidal). When so obtained its activity is destroyed at 55° in three hours. When the protein impurity is present, this temperature does not destroy its activity.

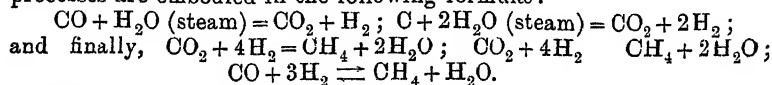
W. D. H.

**Formation of Organic Phosphorus Compounds and their Function in Zymase Fermentation.** LEONID IWANOFF (*Centr. Bakt. Par.*, 1909, ii, 24, 1—12. Compare Abstr., 1907, ii, 191).—The organic phosphorus compound formed during the fermentation of sugar by zymase is apparently a compound of phosphoric acid with a triose which forms a phenylosazone, m. p. 127—128°. The formation of this compound is brought about by means of an easily soluble enzyme, contained in the zymase preparations, here termed synthase. The synthetical enzyme is destroyed in presence of hydrogen cyanide, or when the zymase filtrate is heated. This triose-phosphoric acid is fermented by zymase, forming carbon dioxide, alcohol and inorganic phosphoric acid; it is also fermented by the insoluble portion of zymase, which is quite without action towards dextrose. The stimulation of zymase fermentation by phosphates finds an explanation therefore in the formation of triose-phosphoric acid. The fermentation of dextrose may be considered to take place in three phases: (1) depolymerisation to a triose; (2) coupling of this with phosphoric acid by means of the soluble enzyme synthase; (3) destruction of the triosephosphoric acid by means of the sparingly soluble enzyme of zymase—termed alcoholase—to form carbon dioxide and alcohol.

E. F. A.

## Organic Chemistry.

Some Gas Reactions. M. MAYER, F. HENSELING, V. ALTMAYER, and J. JACOBY (*J. Gasbeleuchtung*, 1909, 52, 166—171, 194—201, 238—245, 282—286, 305—313, 326—328).—An elaboration and continuation of the work of Sabatier and Senderens. The authors describe the preparation of the oxides of carbon and hydrogen, also of pure nickel, cobalt, and iron, for employment as catalysts in the experiments which culminated in the synthesis of methane from its elements. The processes are embodied in the following formulæ:



With carbon monoxide and hydrogen the employment of iron as catalyst yielded only small quantities of methane, this result being attributed to the oxidation of the metal. Experiments with steam instead of hydrogen, and with finely-divided carbon instead of the oxides, were also carried out, and in the latter case very little methane was formed.

A study of the velocity and equilibrium of the reactions under varying conditions showed them to be balanced, and to depend greatly on the physical constants of the reacting substances. Illustrations of the apparatus used, an explanation of the methods employed for calculating the analytical results, and a critical bibliography are also appended.

F. M. G. M.

Apparatus for the Preparation of Acetylene. WILHELM STEINKOPF (*Chem. Zeit.*, 1909, 33, 969).—The calcium carbide is contained in a gauze cylinder suspended in a vessel open at the bottom, and closed above by a cork through which the delivery tube passes. This vessel is suspended in an outer vessel containing water. The lime formed falls to the bottom of the outer vessel. C. H. D.

Electric Transport and Electrolytic Decomposition of Chloroform. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 133—135).—When an emulsion of chloroform in water is placed in the middle vessel of an electric transport apparatus, and subjected to the action of a current, the chloroform migrates towards the anode, where it undergoes decomposition with formation of hydrochloric acid.

T. H. P.

Chlorination of Ethyl Chloride. WILHELM STAEDEL (*J. pr. Chem.*, 1909, [ii], 80, 303—304).—Forty years ago the author found that chlorine and the vapour of ethyl chloride react instantly in direct sunlight, and the product contains ethylidene chloride, but not ethylene

chloride. Twenty years later, V. Meyer found that the interaction of liquid ethyl chloride and antimony pentachloride gave a product containing ethylene chloride, and not ethylidene chloride.

The author now states that his original results are correct (following abstract); by using a mercury vapour lamp and quartz vessels, and liquid chlorine and ethyl chloride, the time of the experiment is very largely shortened. C. S.

**Chlorination of Ethyl Chloride.** JOH. D'ANS and J. KAUTZSCH (*J. pr. Chem.*, 1909, [ii], 80, 305—314).—When approximately equal molecular quantities of chlorine and ethyl chloride are condensed in a quartz vessel cooled by a mixture of ether and solid carbon dioxide, and are exposed, at a distance of 40—50 cm., to the rays of a Heraeus mercury vapour lamp, the product yields by fractionation about 70% of ethylidene dichloride and 10% of ethylene dichloride. When 1.5 mols. of chlorine are used, the lamp must be placed at a distance of 60—70 cm. to prevent explosive reaction; the product contains 50% ethylidene dichloride, and not any ethylene dichloride.

Ethylidene dichloride is more difficultly chlorinated in light than ethylene dichloride; hence the behaviour of the two substances under these conditions is just the converse of their behaviour when chlorinated in the presence of a "carrier" (Meyer and Müller, *Abstr.*, 1892, 577, 1414).

When iodine is added in the preceding experiments, the reaction is retarded to an astonishing degree. Ethyl chloride and iodine trichloride scarcely react at 105°. C. S.

**Preparation of Nitromethane.** II. WILHELM STEINKOFF and GEORG KIRCHHOFF (*Ber.*, 1909, 42, 3438—3440. Compare this vol., i, 78).—More convenient than that described previously is the following method, which proceeds smoothly and yields scarcely any hydrogen cyanide. Chloroacetic acid (500 grams) is dissolved in one litre of water, and neutralised by 280—300 grams of ignited sodium carbonate. The solution is mixed with 300 grams of sodium nitrite in 500 grams of water. About one-fourth of the mixture is placed in a two-litre flask connected to a condenser and also to a water-pump, and is heated to boiling; the remainder of the solution is run in from a dropping funnel at such a rate that a steady evolution of nitromethane is maintained. At the end of the reaction about 250 c.c. of the water are distilled over, and the remainder of the solution in the flask (consisting of sodium carbonate), excepting 100 c.c., is drawn off by the pump, neutralised by chloroacetic acid, mixed with sodium nitrite, and utilised over again. The other end of the condenser is connected to a convenient apparatus for the separation of the nitromethane in the aqueous distillate. The yield of purified nitromethane is about 50%. C. S.

**Action of Nitrogen Trioxide on Tetramethylethylene [ $\beta$ -Dimethyl- $\Delta^2$ -butylene].** NICOLAUS J. DEMJANOFF and K. W. SIDORENKO (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 832—838).—The results of Schmidt (*Abstr.*, 1903, i, 597) are not in accord with those obtained by Demjanoff (*Abstr.*, 1899, i, 845).

On adding an ethereal solution of nitrogen trioxide (from arsenious anhydride and nitric acid) to an ethereal solution of  $\beta\gamma$ -dimethyl- $\Delta^8$ -butylene, the latter being in slight excess, the liquid becomes blue and the following compounds are formed: (1)  $\beta\gamma$ -dinitro- $\beta\gamma$ -dimethylbutane (compare Zelinsky, *J. Russ. Phys. Chem. Soc.*, 1894, 26, 610; Konowaloff, *Abstr.*, 1895, i, 633; Bewad and Pirinsky, *Abstr.*, 1906, i, 393); (2) the compound  $\text{NO}_2 \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{NO}_2$ , m. p. 88—89° (compare Demjanoff, *Abstr.*, 1899, i, 845), apparently mixed with the dinitro-compound,  $\text{NO}_2 \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{NO}_2$ ; on reduction, this mixture, m. p. 101—104°, yields the diamino-compound,  $\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{NH}_2$ , and the hydroxy-amine,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{NH}_2$  (compare Demjanoff, *Abstr.*, 1899, i, 845). T. H. P.

**Ethylene Ozonide.** CARL D. HARRIES and RUDOLF KOETSCHAU (*Ber.*, 1909, 42, 3305—3311. Compare Harries and Haefner, *Abstr.*, 1908, i, 846).—*Ethylene ozonide*,  $\text{C}_2\text{H}_4\text{O}_3$ , may be prepared by the action of ozonised air on a solution of ethylene in methyl chloride at  $-70^\circ$  in the complete absence of water. It is a colourless liquid, b. p. 18°/16 mm., with an unpleasant, intensely pungent odour, and explodes with great violence when heated in a tube or rubbed with a glass rod. Mol.-wt. determinations and the values  $n_D^{17.5} 1.4099$  and  $D_{17.5}^{17.5} 1.2650$  show that the compound has the formula  $\begin{array}{c} \text{CH}_2 \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{O} \end{array} > \text{O}$ . It is decomposed by water according to the two equations:  $\text{C}_2\text{H}_4\text{O}_3 + \text{H}_2\text{O} = 2\text{H} \cdot \text{CHO} + \text{H}_2\text{O}_2$  and  $\text{C}_2\text{H}_4\text{O}_3 = \text{H} \cdot \text{CHO} + \text{H} \cdot \text{CO}_2\text{H}$ .

W. H. G.

**Nitro-derivatives of Glycerol Ether.** EMANUALE PATERNÒ and T. BENELLI (*Gazzetta*, 1909, 39, ii, 312—314).—The authors propose to replace the dinitromonoformin, dinitromonoacetin, etc., added to dynamite in order to lower its freezing point, by the corresponding derivatives in which an alkyl radicle is substituted for the acid radicle. Attempts to find a practicable method of preparing and separating the monomethyl and monoethyl ethers of glycerol were unsuccessful, so that the authors have confined their attention to the dimethyl and diethyl ethers, the nitro-derivatives of which have been prepared.

*Glyceryl dimethyl ether nitrate*,  $\text{NO}_2 \cdot \text{O} \cdot \text{CH}(\text{CH}_2 \cdot \text{OMe})_2$ , prepared by nitrating glycerol dimethyl ether, is a colourless, neutral liquid with a pungent odour, b. p. 180°, m. p.  $-15^\circ$ . It is readily inflammable, but non-explosive, and when added to nitroglycerol in the proportion of 2%, lowers the m. p. from  $-18^\circ$  to  $-34^\circ$ ; even when present to the extent of 10%, it produces no appreciable diminution in the explosive properties of nitroglycerol. Replacement of all or part of the nitroglycerol employed in the manufacture of ballistite by glyceryl dimethyl ether nitrate results in a diminution of the explosive force.

*Glyceryl diethyl ether nitrate*,  $\text{NO}_2 \cdot \text{O} \cdot \text{CH}(\text{CH}_2 \cdot \text{OEt})_2$ , b. p. 168—170° (decomp.), decomposes to such an extent on boiling that the boiling is maintained by the heat generated by the decomposition; it becomes very dense, but does not solidify, at  $-75^\circ$ . T. H. P.

**Physico-chemical Researches on Lecithin and Cholesterol.**  
II. and III. OTTO PORGES and ERNST NEUBAUER (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 193—197. Compare Abstr., 1908, ii, 90).—Researches dealing with the physico-chemical properties of alcoholic and ethereal lecithin and cholesterol solutions.

II. Alcoholic solutions of cadmium chloride have been shown by Strecker to precipitate alcoholic lecithin solutions. Although the precipitate has well crystallised form, its composition, determined by analysis, does not indicate that it is a definite molecular compound; this has been attributed to its instability by several workers. The present work bears on the subject in that the action of salts dissolved in alcohol on alcoholic lecithin solutions has been investigated, and the author considers that the precipitates obtained are not chemical compounds, but of the same nature as the precipitates from aqueous lecithin suspensions. That the solution contains lecithin as a negative colloid is indicated by the reaction with ferric chloride and the precipitation by acid. This conclusion is further supported by the following considerations: Biltz (compare Abstr., 1904, ii, 324) has shown that oppositely charged colloids react together in a typical manner in that they in a certain optimum concentration are precipitated, while excess of either component inhibits precipitation. Ferric chloride solution contains the positive colloid ferric hydroxide. It was found that a 0.1% alcoholic lecithin solution is precipitated by an 0.01*N* ferric chloride solution, less so by one of 0.05*N* strength, whilst 0.2*N*, 0.002*N*, and 0.0005*N* solutions have no effect.

There are certain characteristic differences between the conditions of the lecithin in aqueous and alcoholic suspensions. The latter present a striking similarity to aqueous albumin solutions. In alcoholic solution the state of the lecithin is very like that of a "hydrophylous" colloid in aqueous solution, whilst an aqueous lecithin suspension shows the phenomena peculiar to a "suspension" colloid.

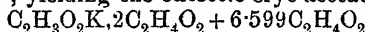
III. Experiments on the precipitation of ethereal lecithin solutions are even more restricted in number than those dealing with alcoholic solutions. Ethereal ferric chloride solution gives, when concentrated, a precipitate, whilst mercuric chloride brings about no change. The presence of lecithin in ether increases in many cases the solubility of other substances therein. Many instances of this are well known, and an explanation of this lies in the fact that a dry ethereal lecithin solution can take up considerable quantities of water in addition to that taken up by dry ether alone. The existence of many "lecithides," it is suggested, may depend on this solubility, and it may also have some bearing on the jecorin question. In conclusion, the author states that similar experiments to the above in alcoholic and ethereal solutions of cholesterol bring about no change, and the conclusion is drawn that cholesterol is in true solution. G. S. W.

**Cryo-acetates of Potassium, Sodium, and Lithium Acetates.**  
ALEXIS VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 753—757).—The author applies the term "cryo-acetates" to potassium, sodium, and lithium acetates united with acetic acid of crystallisation. Potassium or sodium acetate combines with  $1\text{C}_2\text{H}_4\text{O}_2$  and  $2\text{C}_2\text{H}_4\text{O}_2$ , lithium

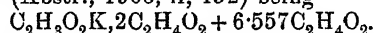
acetate only with  $1C_2H_4O_2$ , the compounds formed being all stable under ordinary conditions. The influence of the atomic weight of the metal on the stability of these compounds is shown by the fact that  $C_2H_3O_2K, 2C_2H_4O_2$  melts ( $112^\circ$ ) without decomposing, whilst  $C_2H_3O_2Na, 2C_2H_4O_2$  decomposes on melting, and lithium acetate yields only the compound  $C_2H_3O_2Li, C_2H_4O_2$ .

The method employed to obtain these compounds free from water, which they retain very persistently, consists in mixing the acetate with a small quantity of glacial acetic acid and repeatedly treating the mixture with acetic acid, the liquid formed being allowed to flow away before each new treatment with the acid.

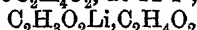
The compound  $C_2H_3O_2K, 2C_2H_4O_2$  reacts with acetic acid at the temperature  $+7.9^\circ$ , yielding the eutectic cryo-acetate,



(compare this vol., ii, 888), the composition calculated by means of Flawitzky's law (Abstr., 1906, ii, 152) being



Similarly, the compound  $C_2H_3O_2Na, 2C_2H_4O_2$  gives the cryo-acetate,  $C_2H_3O_2Na, 2C_2H_4O_2 + 14.55C_2H_4O_2$ , at  $12.1^\circ$ , and the compound



the cryo-acetate,  $C_2H_3O_2Li, C_2H_4O_2 + 8.88C_2H_4O_2$  (calc.  $8.441C_2H_4O_2$ ).

T. H. P.

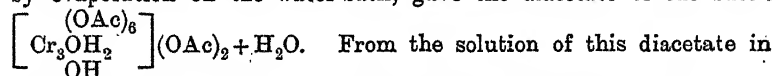
### Salts of a Hexa-acetato(formato)-trichrome Base. II.

RUDOLF WEINLAND and P. DINKELACKER (*Ber.*, 1909, 42, 2997—3018).

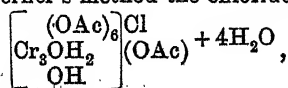
—In a former paper (Abstr., 1908, i, 847) Weinland has described the preparation of primary, secondary, and tertiary salts of a green triacid hexa-acetato-trichromo-base,  $[Cr_3(OAc)_6](OH)_3$ . Shortly after this, Werner (Abstr., 1908, i, 933) gave an account of some salts which he designated as hexa-acetato-diol-trichromo-salts, formulating the chloride, for example, as  $[Cr_3(OAc)_6](OH)_2]Cl + 6H_2O$ . Werner prepared

only primary salts. The present paper gives an account of investigations proving that Werner's and the authors' compounds are identical; according to the former investigations only the platinichlorides were the same, although Werner found  $6H_2O$  and the authors  $5H_2O$ .

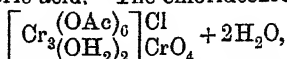
The chloride was first prepared as follows: From a solution of the dichromateacetate the chromic acid was precipitated by lead acetate. The excess of lead was precipitated as sulphide, and the filtrate, by evaporation on the water-bath, gave the diacetate of the base:



dilute hydrochloric acid the chloride was obtained, and found to be identical with that prepared by Werner's method. Both preparations contained  $8H_2O$ , whereas Werner gives  $6H_2O$ . From the chloride made according to Werner's method the chloridacetate,



was prepared by dissolving the former in 50% acetic acid and adding concentrated hydrochloric acid. The chloridechromate,



was also prepared by treating Werner's chloride with chromic acid and concentrated hydrochloric acid. Both these salts were identical with those previously obtained by the authors from the dichromateacetate.

The poly-acidity of the base was further proved by the preparation of the following salts, in addition to those previously described by Werner and the authors. Mono-, di-, and tri-acetates, bromide- and iodide-acetates, sulphate, stannichloride and antimonicchloride, semi-chromateacetate, chromate, bromidechromate, perbromide, a double chloride of the chlorideacetate and ferric chloride, a compound of 3 molecules of the chloride with 1 molecule of the diacetate.

A new method of preparing the base is to heat the green or violet hydrate of chromic chloride, or the violet chromic nitrate, with glacial acetic acid.

A solution of the free base was prepared by the action of silver oxide on a concentrated solution of the chloride. The green filtrate from the silver chloride reacts alkaline, but in a few hours it becomes acid and has the odour of acetic acid. After a long time the solution becomes violet.

Assuming that the secondary and primary salts are hydroxo-salts, the salts are so formulated that the cation of the tertiary contains 2 molecules of water, that of the secondary 1 molecule of water and one hydroxyl group, and that of the primary two hydroxyl groups.

Werner also prepared some salts of a green hexaformato-diol-trichromo-base. The authors show that this base also gives secondary and tertiary salts. The triformate, chloridechromate, and chromate were prepared, the starting point being the monoformate in each case.

This latter compound,  $\left[ \text{Cr}_3 \begin{pmatrix} \text{H} \cdot \text{CO}_2 \\ \text{OH} \end{pmatrix}_6 \right] (\text{H} \cdot \text{CO}_2) + 5\text{H}_2\text{O}$ , can not only be prepared by heating chromium hydroxide with formic acid of sp. gr. 1.15—1.20 (Häussermann, *Abstr.*, 1895, i, 15), but also by warming chromic acid with aqueous formic acid, the latter reaction being similar to that used for the salts of the hexa-acetatotrichromobase.

T. S. P.

**Preparation of Esters of  $\alpha$ -Halogenated Fatty Acids.** BERTHOLD RASSOW and R. BAUER (*J. pr. Chem.*, 1909, [ii], 261—270).

—The various processes for the production of esters of  $\alpha$ -halogenated fatty acids described in the literature have been examined. Auwers and Bernardi's method of treating the free acid with bromine and amorphous phosphorus is the best.  $\alpha$ -Ethylbutyric acid under these conditions yields  $\alpha$ -ethylbutyryl bromide, which is changed by the addition of more bromine to bromo- $\alpha$ -ethylbutyryl bromide. This reacts with alcohol to form *ethyl  $\alpha$ -bromo- $\alpha$ -ethylbutyrate*,  $\text{C}_2\text{H}_5\text{Br} \cdot \text{CO}_2\text{Et}$ , b. 194—196°.

Ethyl  $\alpha$ -hydroxy- $\alpha$ -ethylbutyrate reacts with phosphoric chloride bromide, or with phosphorus bromide, to form, usually, ethyl  $\alpha$ -ethyl- $\Delta^2$ -pentenoate. The elements of hydrogen bromide can be added to the

unsaturated ester by heating it in sealed tubes at  $100^{\circ}$  with a concentrated solution of hydrogen bromide in glacial acetic acid, but it is uncertain whether the halogen enters the  $\alpha$ - or the  $\beta$ -position.

C. S.

**Formation of Butyric Acid from Alcohol under the Influence of the Silent Discharge.** WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 20, 126—135).—Butyric acid is formed from alcohol vapour under the influence of the silent discharge, together with acetaldehyde, formaldehyde, alcohol, and other products. The theory of the formation of these products is discussed by the author, who describes in detail the apparatus employed and the method of isolation. S. B. S.

**Preparation of Fatty Acids and their Anhydrides.** H. FOURNIER (*Bull. Soc. chim.*, 1909, [iv], 5, 920—926. Compare Abstr., 1907, i, 271).—The acids are prepared, as described already (*loc. cit.*), by the oxidation of primary saturated alcohols with potassium permanganate in presence of potassium hydroxide, and the best conditions for securing good yields are given in detail. The anhydrides are prepared by the addition of acetyl chloride to the acid heated at  $120$ — $125^{\circ}$ , the temperature being subsequently raised to  $180^{\circ}$ . The yield of anhydride varies from 55% to 75% of the theoretical.

In the following cases the substances are either new, or new constants are recorded for them. *n*-Valeric acid, b. p.  $86$ — $88^{\circ}/15$  mm., yields an anhydride, b. p.  $110$ — $111^{\circ}/15$  mm.; amide, m. p.  $104$ — $105^{\circ}$ , and anilide, m. p.  $63^{\circ}$ . *iso*Valeric anhydride has b. p.  $102$ — $103^{\circ}/15$  mm.; the anilide has m. p.  $113$ — $114^{\circ}$ . *iso*Hexoic anhydride has b. p.  $130$ — $131^{\circ}/15$  mm., and the anilide, m. p.  $111^{\circ}$ , crystallises in silky needles. *n*-Heptoic anhydride has b. p.  $167$ — $169^{\circ}/20$  mm. *iso*Heptoic acid has b. p.  $212$ — $214^{\circ}$  under atmospheric pressure, and  $107$ — $108^{\circ}/15$  mm.; its anhydride has m. p.  $154^{\circ}/15$  mm., and the amide, m. p.  $103^{\circ}$ , crystallises from water; the anilide has m. p.  $75^{\circ}$ . T. A. H.

**Hydrolysis of Fats and Oils.** III. J. KELLNER (*Chem. Zeit.*, 1909, 33, 993. Compare this vol., i, 548).—Saponification of palm kernel oil with calcium oxide is like the saponification by alkali, a quadrimolecular reaction. The hydrolysis of palm oil by hydrochloric acid appears to proceed both as a uni- and a bi-molecular reaction, both mono- and di-glycerides being formed. L. DE K.

**Linoleic Acid.** ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1909, 62, 410—421. Compare Hazura, Abstr., 1887, 359; Farnsteiner, *ibid.*, 1899, ii, 705).—Pure methyl linoleate,  $C_{19}H_{34}O_2$ , can be obtained by the action of zinc and methyl alcohol containing a small amount of hydrogen chloride on the tetrabromide (m. p.  $114$ — $115^{\circ}$ ). It can be extracted with light petroleum (b. p.  $30$ — $50^{\circ}$ ) and distilled under diminished pressure. It has b. p.  $207$ — $208^{\circ}/11$  mm.,  $211$ — $212^{\circ}/16$  mm., and  $221$ — $224^{\circ}/35$  mm.,  $D_4^{20}$  0.8886, and iodine number 172 (Theory, 172.8). When hydrolysed with cold alcoholic potassium hydroxide the ester

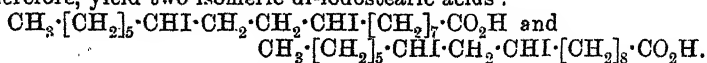
yields pure linoleic acid, which has b. p.  $228^{\circ}/14$  mm. and  $D_4^{18}$  0.9026. When brominated in different solvents, the pure acid does not give more than a 50% yield of the crystalline tetrabromide. A syrupy additive product is always formed, and this may be a stereoisomeric tetrabromide or merely impure crystalline tetrabromide. When reduced, this oil yields linoleic acid.

When oxidised with alkaline permanganate, linoleic acid yields sativic acid, m. p.  $171-173^{\circ}$  (Hazura, Abstr., 1888, 817), together with a small amount of a substance insoluble in benzene. J. J. S.

**Linolenic Acid and Linseed Oil.** ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1909, 62, 422-431. Compare Hazura and Friedrich, Abstr., 1887, 798; Hehner and Mitchell, *ibid.*, 1898, ii, 190; Erdmann and Bedford, this vol., i, 357).—Pure linolenic acid has been investigated in much the same manner as linoleic acid (preceding abstract). The methyl ester, prepared from linolenic acid hexabromide, is a clear, colourless liquid with b. p.  $207^{\circ}/14$  mm. The acid has b. p.  $230-232^{\circ}/17$  mm. and  $D_4^{18}$  0.9141. When brominated in glacial acetic acid solution, the acid yields some 25% of the crystalline hexabromide, m. p.  $181-182^{\circ}$ . The oily by-product appears to be a tetrabromide,  $C_{18}H_{30}O_2Br_4$ , but when the bromine reacts for a longer time an oily hexabromide is formed.

These oils when reduced yield linolenic acid, which yields a mixture of solid and oily hexabromides (compare Erdmann and Bedford, *loc. cit.*). When oxidised with potassium permanganate, the acid yields isolinolenic acid, m. p.  $171-173^{\circ}$  (Hazura:  $173-175^{\circ}$ ), and linusic acid, m. p.  $201-203^{\circ}$ . The conclusion is drawn that there is no evidence for the presence of an isolinolenic acid in linseed oil, or in the acid obtained by reducing the hexabromide. J. J. S.

**Transformations of Ricinoleic Acid.** BRONISLAW F. CHONOWSKY (*Ber.*, 1909, 42, 3339-3356).—The action of hydriodic acid on ricinoleic acid yields di-iodostearic acid,  $C_{18}H_{34}O_2I_2$ , and not iodo-stearidinic acid, as was stated by Claus (Abstr., 1877, ii, 314). Reduction of di-iodostearic acid by means of zinc dust and acetic acid yields only stearic acid; the halogen atoms of the di-iodo-acid are hence not situated at neighbouring carbon atoms, since, with such an arrangement, carbon atoms would be separated and an oleic acid formed. This reaction confirms the view that ricinoleic acid contains an alcoholic hydroxyl group combined with the twelfth carbon atom, and that the double linking is situated between the ninth and tenth carbon atoms. The action of hydriodic acid on ricinoleic acid should, therefore, yield two isomeric di-iodostearic acids:



The action of alcoholic potassium hydroxide on di-iodostearic acid yields an acid,  $C_{18}H_{32}O_2$ , which is isomeric with linoleic acid, and can also be obtained by the action of anhydrous zinc chloride on zinc ricinoleate; the barium and silver salts were analysed. When treated with bromine, this acid yields tetrabromostearic acid,  $C_{18}H_{32}O_2Br_4$ , and

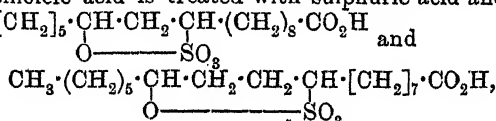
on oxidation with permanganate it gives a resin from which only azelaic acid could be separated.

The action of zinc oxide on di-iodostearic acid yields: (1) a mixture, m. p. 108—114°, of two isomeric oxyoleic or glycidic acids, the oxygen atom in one uniting the ninth and twelfth, and in the other the tenth and twelfth carbon atoms; the *sodium*, *silver*, and *barium* salts of these mixed acids were analysed; (2) an acid with two double linkings or one triple linking, mixed with a small proportion of other acids formed by the decomposition of di-iodostearic acid.

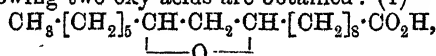
The action of moist silver oxide on di-iodostearic acid, like that of zinc oxide, results in the separation of hydrogen iodide, in addition to replacement of iodine by hydroxyl, a *dihydroxystearic acid*,

$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_8 \cdot \text{CO}_2\text{H}$ ,  
m. p. 116—117°, solidifying point 113—114°, being formed; the *silver*, *barium*, and *sodium* salts of this acid were analysed, and the acetyl derivative prepared. Accompanying this acid are an acid resembling linoleic acid which does not solidify, and small proportions of acids formed by the decomposition of the di-iodostearic acid.

When ricinoleic acid is treated with sulphuric acid and the sulpho-acids,



thus obtained boiled with water and hydrolysed with alkali hydroxide, the following two oxy-acids are obtained: (1)



m. p. 108—109°, which forms a crystalline *diacetyl* derivative,  $\text{C}_{22}\text{H}_{40}\text{O}_6$ ; hydrolysis of the latter with alcoholic potassium hydroxide yields a dihydroxystearic acid, m. p. 115—116°, identical with that obtained by the action of moist silver oxide on di-iodostearic acid; (2)  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$ , m. p. 73—74°, which

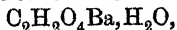
does not react so readily as the isomeric oxy-acid; when treated with acetic anhydride, and the resultant product hydrolysed with alcoholic potassium hydroxide and decomposed by means of hydrochloric acid, it gives a thick oil.

T. H. P.

**Evolution of Hydrogen Occurring when Glyoxylic Acid is Warmed with Barium Hydroxide.** WILHELM TRAUBE (*Ber.*, 1909, 42, 3295—3297).—Hydrogen is evolved when a solution of a glyoxylate is warmed with an excess of barium hydroxide (compare *Abstr.*, 1908, i, 75), probably owing to the occurrence of the reaction:  $\text{CH}(\text{OH})_2 \cdot \text{CO}_2\text{H}$  or  $\text{CHO} \cdot \text{CO}_2\text{H} + \text{H}_2\text{O} = \text{CO}_2\text{H} \cdot \text{CO}_2\text{H} + \text{H}_2$ . Part of the glyoxylic acid is decomposed, however, with the formation of glycollic acid and oxalic acid, the volume of hydrogen evolved depending largely on the proportion of barium hydroxide present in the solution.

The addition of barium hydroxide solution to a solution of barium glyoxylate produces a flocculent precipitate, which is at first soluble in

acetic acid, but quickly passes into a crystalline powder insoluble in this reagent. The latter substance is a *basic barium glyoxylate*,



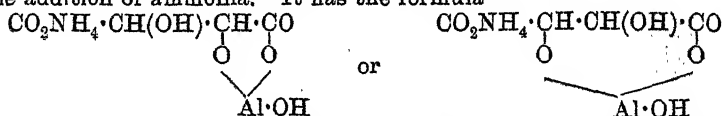
and liberates hydrogen when boiled with water.

W. H. G.

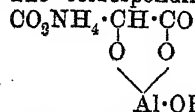
**Complex Organic Aluminium Compounds.** JOSEF HANUŠ and OT. QUADRAT (*Zeitsch. anorg. Chem.*, 1909, 63, 306—317).—The formation of complex aluminium compounds, from which the metal is not precipitated by ammonia, depends on the number of carboxyl as well as of hydroxyl groups. Glyceric acid and glycerol only form complexes when the concentration is high, whilst malic and tartronic acids form complexes very readily. There is for each substance a limiting concentration at which precipitation by ammonia no longer takes place. Amino-, bromo-, and methoxy-succinic acids are without action, as are tartaric anhydride and malic hydrazide.

A  $N/5$  solution of aluminium sulphate, acidified with sulphuric acid, is used, 20 c.c. being taken for each experiment, and varying quantities of the  $N/5$  organic solution added. Water is added to 85 c.c., the solutions rapidly boiled, and 15 c.c. of ammonia added. The quantity of the organic solution which just prevents the production of an opalescence is noted.

The tartaric acid compound may be isolated by using aluminium nitrate instead of the sulphate, and precipitating with alcohol after the addition of ammonia. It has the formula



The corresponding compound from tartronic acid has the formula



. It was not found possible to isolate the

corresponding compounds of malic and citric acids.

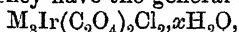
C. H. D.

**Complex Iridium Compounds.** Iridiodichloro-oxalates. MAURICE VÉZES and ALEXIS DUFFOUR (*Bull. Soc. chim.*, 1909, [iv], 5, 869—872. Compare *Proc. verb. Soc. Sci. Bordeaux*, 1901).—*Potassium iridiodichloro-oxalate*,  $\text{K}_3\text{Ir}(\text{C}_2\text{O}_4)_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ , obtained by double decomposition between potassium iridosochloride or iridichloride and potassium oxalate, occurs in monoclinic crystals ( $a:b:c=1.1972:1:1.1996$ ;  $\beta=80.19^\circ 40''$ ), which affect polarised light and have a pomegranate-red colour, and is stable in air and in water, even on boiling. The salt is partly dehydrated at  $100^\circ$ , and decomposes at  $245^\circ$ , forming iridium, potassium iridate, carbonate, and chloride, and evolving carbon dioxide and monoxide.

A solution of the salt gives no reaction for chlorides or oxalates, but with silver nitrate yields a red precipitate of *silver iridiodichloro-oxalate*,  $\text{Ag}_3\text{Ir}(\text{C}_2\text{O}_4)_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ , which separates from solution in warm water in ruby-red crystals. The silver salt is unaffected by light, and

is stable in cold water, but when heated in water slowly decomposes, giving a precipitate of silver chloride and oxalate. It is dehydrated at 130—140°, and decomposes at 270°, leaving a residue of iridium, silver chloride and oxide (?). The silver salt reacts readily with chlorides, and can thus be used for the preparation of other iridochloro-oxalates (see succeeding abstract). T. A. H.

**Complex Iridium Compounds.** Iridiodichloro-oxalic Acid and its Salts. ALEXIS DUFFOUR (*Bull. Soc. chim.*, 1909, [iv], 5, 872—876. Compare preceding abstract).—The preparation and properties of the acid and of a number of its salts are described. The salts crystallise well, often in isomorphous forms, and the crystals affect polarised light. They have the general formula



are all red in colour, mostly very soluble in water and all insoluble in alcohol or ether, and when heated are dehydrated with difficulty and usually decompose at 200—230°, yielding black residues containing metallic iridium and a mixture of chloride and carbonate of the second metal present.

*Iridiodichloro-oxalic acid*,  $\text{H}_3\text{Ir}(\text{C}_2\text{O}_4)_2\text{Cl}_2, 4\text{H}_2\text{O}$ , obtained by the action of hydrochloric acid on the silver salt suspended in warm water (see preceding abstract), crystallises in red, very deliquescent needles, is tribasic, acid to litmus or phenolphthalein, decomposes carbonates in solution, and changes slowly when kept or more rapidly when heated, either when dry or in aqueous solution, forming oxalic acid and leaving the iridium as a red soluble compound, not yet investigated.

The *rubidium*, *caesium*, and *ammonium* salts crystallise in hexagonal lamellae with  $1\text{H}_2\text{O}$ . The *lithium* and *sodium* salts crystallise with  $8\text{H}_2\text{O}$ , and fuse in their water of crystallisation at 48° and 62° respectively; the former is very deliquescent, and both are readily soluble in water. The *thallium* salt forms prismatic needles, is anhydrous, and resembles the silver salt in being sparingly soluble in cold water; at 200° it blackens, and at a red heat the thallium in the residue volatilises in white fumes. T. A. H.

**Action of Alcohols, Acids, and Amines on Methyl Oxomalonate.** RICHARD S. CURTISS and F. GRACE C. SPENCER (*J. Amer. Chem. Soc.*, 1909, 31, 1053—1057. Compare Anschütz and Parlato, *Abstr.*, 1893, i, 193).—*Methyl oxomalonate*,  $\text{CO}(\text{CO}_2\text{Me})_2$ , b. p. 106°(uncorr.)/40 mm., obtained in a yield of 92% by leaving methyl dihydroxymalonate in contact with phosphoric oxide for two hours, is a yellowish-green oil, has  $D_{27}^{20}$  1.2464, and is rapidly reconverted into the dihydroxymalonate on exposure to the air.

Ethyl alcohol unites with methyl oxomalonate to form the *ethyl ether* of methyl dihydroxymalonate,  $\text{OH}\cdot\text{C}(\text{CO}_2\text{Me})_2\cdot\text{OEt}$ , m. p. 58°, which forms colourless needles. Methyl and propyl alcohols also react with methyl oxomalonate, yielding thick oils resembling glycerol, which are converted by moist air into the respective alcohols and methyl dihydroxymalonate.

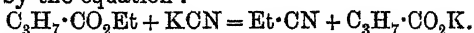
When methyl oxomalonate is treated with dry hydrogen chloride, *methyl chlorotartrate*,  $\text{OH}\cdot\text{CCl}(\text{CO}_2\text{Me})_2$ , m. p. about 42°, is produced,

which forms colourless crystals and is very unstable, being rapidly converted into methyl dihydroxymalonate on exposure to moist air; ethyl alcohol reacts with this compound with formation of the ethyl ether of methyl dihydroxymalonate. Hydrogen bromide combines with methyl oxomalonate in a similar manner to produce *methyl bromotartronate*, m. p.  $30^{\circ}$  (decomp.), which dissociates at  $40^{\circ}$  into hydrogen bromide and the keto-ester. Hydrogen iodide also reacts with methyl oxomalonate, but the product is very unstable and has not been analysed.

When an ethereal solution of aniline is added gradually to methyl oxomalonate, *methyl anilinetartronate*,  $\text{NPh}\cdot\text{C}(\text{CO}_2\text{Me})_2\cdot\text{OH}$ , m. p.  $102^{\circ}$ , is obtained as a white, crystalline substance which is readily decomposed by hot water into aniline and methyl dihydroxymalonate. By the action of phosphoric oxide on this compound, *methyl phenyliminomalonate*,  $\text{NPh}\cdot\text{C}(\text{CO}_2\text{Me})_2$ , is produced, and is now being investigated.

Ammonia and urethane also form crystalline additive products with methyl oxomalonate. E. G.

**Action of Potassium Cyanide on *iso*Butaldehyde.** K. A. TAIPALE (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 815—832. Compare Claisen, Abstr., 1893, i, 8; 1899, i, 667; Kohn, Abstr., 1899, i, 328).—From a study of the products obtained by the action of potassium cyanide on *isobutaldehyde* (1) without solvent, (2) in ethereal and (3) in alcoholic solution, the author concludes that when potassium cyanide does not undergo hydrolysis, it acts on *isobutaldehyde* in the same way as on other aliphatic aldehydes, and in the same way as other alkaline condensing agents act. The formation of octylene glycol is a secondary reaction, and consists of a double exchange between the condensation products of the aldehyde and the alcoholic solvent under the influence of the potassium cyanide. One of the products of the action of potassium cyanide on *isobutaldehyde* in ethyl alcohol consists apparently of propionitrile, formed as a result of an accessory reaction represented by the equation:



The formation of *isobutaldol* cyanohydrin or the isomeric imino-ether, observed by Kohn and by Claisen (*loc. cit.*), is due to the hydrolysis of the potassium cyanide, these investigators studying the course of the reaction in presence of water; in all probability the cyanohydrin or imino-ether results from the action of hydrocyanic acid on the *isobutaldol* first formed. T. H. P.

**Tautomerism of Aliphatic Ketones.** ADRIANO OSTROGOVICH (*Ber.*, 1909, 42, 3186—3187).—Polemical. The author draws attention to discrepancies in the analytical data in Hâncu's paper on this subject (compare this vol., i, 364). The results of Hâncu's determinations of acetyl groups, stated by him to be in close agreement with the theory, actually work out to 149% and 195% of the esters analysed respectively. R. V. S.

**Action of Sodium on Acetone.** MAURICE DELACRE (*Bull. Soc. chim.*, 1909, [iv], 5, 884—889).—Since in the action of sodium on

acetone in presence of a solution of potassium hydroxide only 14% of pinacone and 10% of isopropyl alcohol are obtained, and these materials are generally regarded as the products of the principal reactions which take place, the author has investigated quantitatively, in large scale operations, the destination of that part of the acetone still unaccounted for. The results show that losses occur by (1) evaporation of acetone during the action; (2) the formation of water; (3) the production of phorone and other more complex condensation products; (4) the formation of mesityl oxide. Denigés' statement (Abstr., 1904, i, 706) that dimethylisopropylcarbinol is formed in this reaction could not be confirmed, but evidence of the formation of a ketonic substance boiling at 114° was obtained. Further, no propyl alcohol is produced.

T. A. H.

So-called  $\psi$ -Dichloroacetone, an Alleged Isomeride of Dichloroacetone. THEODOR POSNER and KARL RÖHDE (*Ber.*, 1909, 42, 3233—3242).—The object of this work is to clear up the uncertainties and contradictions which exist in the literature regarding the chlorine substitution products of acetone.

The authors find that oxidation of  $\alpha$ -dichlorohydrin, and also chlorination of acetone, lead to one and the same substance, *s*-dichloroacetone, which does not react with potassium phthalimide in the way formerly supposed, but yields only phthalimide. Hence Cloez's  $\psi$ -dichloroacetone and  $\psi$ -phthaliminoacetone do not exist. Further, the chlorination of acetone yields both *symmetrical* and *asymmetrical* dichloroacetone, but no polymeric dichloroacetones; the latter are therefore to be erased from the literature.

The product obtained by chlorinating acetone by the method of Fritsch (Abstr., 1894, i, 490) yielded on distillation a main fraction, which, on further purification, had b. p. 118—120°. A smaller portion of the oil distilled at 160—178°, and was fractionated until it had b. p. 167—175°. After a time it crystallised, and the separated crystals were white, had b. p. 172.6—173°/748 mm. (corr.), and m. p. 43°;  $D_4^{20}$  1.3843;  $n_D^{20}$  1.47223;  $M_D$  25.71 (ketonic form requires 25.99); molecular dispersion 0.708 (ketonic form requires 0.702, pseudo-form 0.625). The method of Hörmann (Abstr., 1881, 248) was found to give only 6% yield; it was therefore modified by shaking the distillate with ether, and extracting the dichloroacetone by shaking the ethereal solution with sodium hydrogen sulphite. The ether is then distilled off and the residual oil again subjected to oxidation, and so on until all the dichlorohydrin is oxidised. The distillate obtained on decomposing the hydrogen sulphite solutions yielded crystals of m. p. 43° and b. p. 173—173.4°/759 mm. (corr.);  $D_4^{20}$  1.3809;  $n_D^{20}$  1.47144;  $M_D$  25.72; molecular dispersion 0.725.

*s*-Diphtaliminoacetone was prepared by Gabriel and Posner's method (*loc. cit.*), and had the correct m. p., 268°. Its ketonic nature follows from the formation of an *oxime*, which forms colourless crystals of m. p. 217°. Numerous repetitions of the reaction between potassium phthalimide and pure *s*-dichloroacetone yielded nothing but phthalimide. It was also not possible to obtain the compound previously

described by Posner, even when the raw distillate obtained in the oxidation of dichlorohydrin was used instead of pure dichloroacetone. An investigation of a sample of the  $\psi$ -diphthaliminoacetone formerly described by Posner indicated that it was a mixture of ordinary  $s$ -diphthaliminoacetone with phthalimide.

*Optical Behaviour of  $\alpha$ -Dichlorohydrin and of Epichlorohydrin.*—Commercial  $\alpha$ -dichlorohydrin was repeatedly fractionated; a small middle portion of a constant-boiling fraction then gave the following figures:  $D_4^{17}$  1.3506;  $n_D^{18.9}$  1.480245;  $M_D$  27.15; mol. dispersion 0.670. The ketonic formula requires  $M_D$  27.33; mol. dispersion 0.703. R. V. S.

**Preparation of Pure Ketones by means of Acetoacetic Ester.** ARTHUR MICHAEL and KARL WOLGAST (*Ber.*, 1909, 42, 3176—3177).—The interaction of alkyl halides and sodioacetoacetic ester produces a mixture of mono- and di-alkylacetoacetic esters, from which the former can only be obtained pure by chemical means (Michael, *Abstr.*, 1905, i, 564). Ceresole showed (*Abstr.*, 1883, 41) that monoalkylacetoacetic esters are readily saponified by aqueous alkali hydroxides in the cold, whilst the dialkyl derivatives, with the exception of dimethylacetoacetic ester, are not attacked. This difference may be applied to the preparation of pure ketones, and obviates the necessity of starting with pure monoalkylacetoacetic esters. The mixture of esters is freed from acetoacetic ester by shaking with ammonia, fractionated once, then shaken for fifteen minutes with excess of 5% potassium hydroxide. The alkaline solution is separated from the insoluble oil and acidified with dilute hydrochloric acid. The ketone is isolated by distillation.

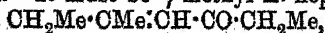
In the case of methyl propyl ketone (from ethylacetoacetic ester), the distillate contains alcohol which cannot be removed by fractionation. The ketone is therefore separated as the bisulphite compound.

R. V. S.

**Electrolytic Reduction of Methyl *iso*Amyl Ketone to *iso*Heptane.** JULIUS TAFEL (*Ber.*, 1909, 42, 3146—3148. Compare this vol., i, 545).—If lead cathodes are used in the reduction, as in the case of the acetoacetic esters, the yield is reduced to 25%, owing to the formation of organic lead compounds. The yield is now raised to 83.5% by employing an apparatus similar to that used for the reduction of acetoacetic esters, but containing as cathode a hollow cylinder of cadmium which can be cooled with water. The product after purification showed b. p. 89.1—89.6°/748 mm., in agreement with the value previously found for the pure hydrocarbon by Purdie (*Trans.*, 1881, 39, 464). The author proposes to employ the method extensively for the preparation of hydrocarbons.

R. V. S.

**Action of Calcium Carbide on Some Ketones. II.** F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1909, [iv], 5, 950—952).—The unsaturated ketone described already (*Abstr.*, 1908, i, 854), obtained by the action of calcium carbide on butanone, has  $n_D^{15}$  1.4497, and yields a *semicarbazone*, m. p. 114—115°, crystallising in colourless needles. It must be  $\gamma$ -methyl- $\Delta^7$ -heptene- $\epsilon$ -one,



since on reduction by Sabatier and Senderens' method it yields  $\gamma$ -methylheptane- $\epsilon$ -one,  $\text{CH}_3\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Me}$ . The latter is a pleasant-smelling, colourless liquid, having  $D_{25}^{25}$  0.820,  $n_D^{25}$  1.4124, b. p. 153—155°/760 mm., and yielding a semicarbazone, m. p. 102°, crystallising in colourless prisms.

$\beta$ -Methylpentan- $\delta$ -one reacts with calcium carbide to form  $\beta\delta$ -tri-methyl -  $\Delta^8$  - nonene -  $\zeta$  - one,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}_2$ ,  $D_{18}^{18}$  0.838,  $n_D^{18}$  1.4491, and b. p. 217—219°/760 mm., which yields a viscous oxime, b. p. 143—146°/17 mm., and, on reduction, furnishes the corresponding saturated ketone as a pleasant-smelling liquid, having  $D_{18}^{18}$  0.820,  $n_D^{18}$  1.4262, b. p. 210—212°/760 mm., which does not combine with sodium hydrogen sulphite, but yields a liquid oxime, b. p. 138—140°/15 mm.

Mesityl oxide reacts with calcium carbide, but does not give the expected ketone,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CMe}_2$ , but a mixture of products having  $D_{17}^{17}$  0.937,  $n_D^{17}$  1.5057, and b. p. 238—242°/741 mm., which furnishes two semicarbazones, the one gummy and the other, m. p. 165—166°, crystallising in colourless prisms. On reduction the mixture gives a colourless liquid of unpleasant odour and b. p. 200—230°, from which no definite product could be isolated.

T. A. H.

**The Fission of Sugars. V. The Reversal of the Sugar Synthesis.** WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 20, 516—522. Compare Abstr., 1908, i, 715, 764; this vol., i, 352, 456).—The author discusses the conditions which cause the formation of a pentose and formaldehyde from a hexose, and the reverse reaction of the formation of a hexose from a pentose and formaldehyde. S. B. S.

**Action of Fehling's Solution on Maltose.** W. LEE LEWIS (*Amer. Chem. J.*, 1909, 42, 301—319).—An account is given of an investigation of the products of oxidation of maltose by Fehling's solution. The results show that the proportions of the acids produced, namely, carbonic, formic, hexonic, and probably glyceric and trihydroxybutyric, differ considerably from those obtained by Nef (Abstr., 1908, i, 5) with dextrose, lævulose, and mannose, and that a new hexonic acid, probably  $\alpha$ -hydroxymethyl- $d$ -ribonic acid, is formed in place of  $\alpha$ -hydroxymethyl- $d$ -arabonic acid. Further, whilst mannose, dextrose, and lævulose yield  $d$ -gluconic acid and traces of  $d$ -mannonic acid, maltose gives glucosido- $d$ -mannonic acid only (compare Nef, *loc. cit.*). Another important point of difference between the oxidation of mannose, dextrose, and lævulose and that of maltose is that, whilst the former sugars yield large amounts of glyceric and trihydroxybutyric acids, it was not possible in the case of maltose to prove the presence of any monobasic acids containing three or four carbon atoms. It is evident that maltose is not appreciably hydrolysed into 2 mols. of dextrose, since the chief oxidation products are glucosido-monobasic acids, but it is possible that it may be converted to a small extent into 2 mols. of dextrose before oxidation takes place.

By the oxidation of 136.8 grams of anhydrous maltose, there were produced 10.6 grams of carbon dioxide, 4.74 grams of formic acid, and 132.8 grams of non-volatile substances, consisting chiefly of glucosido-

acids. The latter, on hydrolysis, gave 47.5 grams of dextrose and 82.35 grams of non-volatile acids, containing 0.35 gram of oxalic acid, 3.92 grams of glycollic acid, 30.25 grams of *d*-mannonolactone, 10.5 grams of  $\alpha$ -hydroxymethyl-*d*-ribonic acid, and 37 grams of acids which were not identified.

*$\alpha$ -Hydroxymethyl-*d*-ribonic acid*, m. p. 183—186°, forms flat, transparent plates, and is soluble in 10 parts of boiling water, but only sparingly in cold water. The *phenylhydrazide*, m. p. 179—183°, has  $[\alpha]_D + 8.38^\circ$ . The *calcium* salt forms small cubes, and has  $[\alpha]_D + 11.98^\circ$ .

It appears probable that only two hexonic acids, namely, *d*-mannonic and  $\alpha$ -hydroxymethyl-*d*-ribonic acids, are produced by the hydrolysis of the glucosido-acid formed by the oxidation of maltose with Fehling's solution. Both these acids must therefore be formed by an unsymmetrical benzilic acid rearrangement from 1:2-maltosone and 2:3-maltosone respectively (Nef, *loc. cit.*). 1:2-*d*-Glucosone, the intermediate product of the oxidation of dextrose, *d*-fructose, and *d*-mannose, however, gives mainly *d*-gluconic acid, together with small quantities of *d*-mannonic acid. In order to test these conclusions, a study has been made of the behaviour of alkali hydroxides towards *d*-glucosone and *d*-maltosone, but the results cannot be regarded as decisive.

E. G.

**Cellulose Esters.** R. G. WOODBRIDGE, jun. (*J. Amer. Chem. Soc.*, 1909, 31, 1067—1071).—*Cellulose tripropionate*, prepared by the action of propionic anhydride on cellulose in presence of sulphuric acid or zinc chloride, closely resembles the acetate, but can be distinguished from the latter by its solubility in ethyl acetate. A study has also been made of cellulose formate, and the results obtained accord with those of Berl and Smith (*Abstr.*, 1907, i, 289), but do not confirm those of Bemberg (*Abstr.*, 1908, i, 321).

E. G.

**Pectins.** A. WILHELMJ (*Zeitsch. Ver. deut. Zuckerind.*, 1909, 895—915).—Pectins, under the influence of moulds, are broken down into optically active arabinose. Freshly prepared pectin solutions likewise yield arabinose when hydrolysed with dilute acids. In years when the beets become mouldy, it is possible that sugar may in this way be formed from the pectins and so affect the accuracy of the sucrose estimations made in the ordinary manner. Hydrolysis of the pectins also takes place when the wet beets are heated, laevorotatory compounds being formed which are not precipitated by lead acetate. The amount formed depends on the temperature and time of heating. Lime produces a copious precipitate in the cold aqueous extract of beets which have been heated after the complete extraction of the sugar. The filtrate, which is laevorotatory, contains three calcium salts, probably those of a saccharate of arabinose, of a  $\gamma$ -hydroxy-acid or its lactone, and of the metapectic acid described by Scheibler. All these yield arabinose on hydrolysis. The calcium oxide precipitate is in part soluble in acetic acid; this fraction is laevorotatory, and is probably the *l*-parapectic acid described by Weisberg.

The residue is partly soluble in hydrochloric acid; this portion is

precipitated by alkalis, and is remarkable in being very resistant to hydrolysis and yielding no arabinose. It is evidently a pectin residue from which the arabinose-yielding group has already been eliminated. The residue insoluble in hydrochloric acid is an acid, probably the parapectic acid of Herzfeld. This is regarded as the mother substance of the products just described, and yields them when hydrolysed.

E. F. A.

**Periodides of Organic Bases.** A. LINARIX (*J. Pharm. Chim.*, 1909, [vi], 30, 241—247).—New *periodides* of the following bases are described. They crystallise well, and have the usual properties of the periodides.

*Ethylenediamine*,  $B, 2HI, I_4$ , m. p.  $218^\circ$ ; *piperazine*,  $B, 2HI, I_4, 3H_2O$ , m. p.  $283^\circ$  (the *anhydrous* form melts at  $280^\circ$ ); *benzidine*,  $B, 2HI, I_4$ , m. p.  $298^\circ$ ; *piperidine*,  $B, HI, I_3$ , m. p.  $45^\circ$ , and  $B, HI, I_4$ , m. p.  $35^\circ$ ; *pilocarpine*,  $B, HI, I_3$ , m. p.  $148^\circ$ , and  $B, HI, I_4$ , m. p.  $135^\circ$ ; *ethylmorphine*,  $B, HI, I_3$ , m. p.  $150^\circ$ , and *xanthine*,  $B, HI, I_3$  (does not melt when heated).

In the case of the benzidine hydriodide periodide, the usual method of estimating the "external" iodine (*loc. cit.*) is inapplicable, as the substance is insoluble in alcohol, but good results were obtained by dissolving the periodide in a solution of potassium iodide in a mixture of water and alcohol and titrating with sodium thiosulphate.

T. A. H.

**The Formation of Nitrogenous Compounds from Nitrogen and Alcohol under the Influence of the Silent Discharge.** WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 20, 136—142).—Under the conditions of experiment described, ammonium formate and hexamethylenetetramine were formed.

S. B. S.

**Action of Calcium Oxide on Hydrazine Hydrate.** ARTHUR STÄHLER (*Ber.*, 1909, 42, 3018—3019).—When hydrazine hydrate is mixed with about three times its weight of calcium oxide, partly in small lumps and partly in the form of powder, the mixture becomes heated to about  $120^\circ$ , and after a time the lumps disintegrate and the whole forms a dry powder. On raising the temperature, a distillate is obtained above  $150^\circ$ ; this at first consists of pure hydrazine, subsequently of hydrazine containing a little ammonia.

Probably a solid solution of hydrazine in calcium oxide is formed, or an additive compound,  $Ca(ON_2H_5)_2$ , which is subsequently dissociated into calcium hydroxide and hydrazine.

E. F. A.

**Synthesis of Polypeptides: Derivatives of *iso*Leucine. I.** EMIL ABDERHALDEN, PAUL HIRSCH, and JOSEF SCHULER (*Ber.*, 1909, 42, 3394—3411).—The authors have prepared a number of polypeptides derived from *dl*- and *d*-isoleucine (compare Brasch and Friedmann, *Abstr.*, 1908, i, 607; Ehrlich, *Abstr.*, 1908, i, 396).

*Chloroacetyl*-*dl*-isoleucine,  $CH_2Cl \cdot CO \cdot NH \cdot CH(CO_2H) \cdot CHMeEt$ , forms crystals, m. p.  $105$ — $106^\circ$  (corr.).

*Glycyl*-dl-isoleucine,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$ , prepared by the action of ammonia on the preceding compound, was not obtained crystalline; it turns brown at  $215^\circ$  and sinters at  $219^\circ$ , m. p.  $242^\circ$  (corr.).

dl- $\alpha$ -Bromoisohexoyl-dl-isoleucine,

$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CHMeEt}$ , prepared from  $\alpha$ -bromoisohexoyl chloride and dl-isoleucine dissolved in sodium hydroxide solution, sinters at  $135^\circ$ , m. p.  $146$ — $149^\circ$  (corr.).

dl-Leucyl-dl-isoleucine,

$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt} (+ \text{H}_2\text{O}?)$ , turns brown at  $250^\circ$ , m. p.  $262$ — $263^\circ$  (corr.).

d- $\alpha$ -Bromo- $\beta$ -methylvaleric acid,  $\text{CHMeEt} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$ , prepared by the action of bromine on l-isoleucine hydrobromide in a current of nitric oxide, softens at  $30^\circ$ , m. p.  $39^\circ$ ,  $[\alpha]_D^{20}$  in benzene +  $26.48^\circ$  ( $\pm 0.2^\circ$ ). On treatment with aqueous ammonia it is converted into l-isoleucine.

d- $\alpha$ -Bromo- $\beta$ -methylvaleryl chloride,  $\text{CHMeEt} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{Cl}$ , obtained by the action of thionyl chloride on the corresponding acid, has b. p.  $67^\circ/3$  mm.

d- $\alpha$ -Bromo- $\beta$ -methylvalerylglycine,

$\text{CHMeEt} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , crystallises from water in flocculent aggregates of needles, sinters at  $85^\circ$ , m. p.  $91$ — $92^\circ$  (corr.),  $[\alpha]_D^{20} + 64.42^\circ$  ( $\pm 0.2^\circ$ ).

d-iso-Leucylglycine,  $\text{CHMeEt} \cdot \text{CH}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , has m. p.  $162^\circ$ ,  $[\alpha]_D^{20} + 33.59^\circ$  ( $\pm 0.2^\circ$ ).

Chloroacetyl-d-isoleucine,  $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$ , has m. p.  $74$ — $75^\circ$ ,  $[\alpha]_D^{20} + 25.0^\circ$  ( $\pm 0.2^\circ$ ).

Glycyl-d-isoleucine,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$ , crystallises from aqueous alcohol in shining leaflets, m. p.  $262^\circ$  (corr.; decomp.),  $[\alpha]_D - 14.7^\circ$  ( $\pm 0.4^\circ$ ).

Glycyl-d-isoleucine anhydride, [3 : 6-diketo-2-sec.-butylpiperazine],  $\text{CH}_2 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CH} \cdot \text{CHMeEt}$ , crystallises in spherical aggregates of needles, m. p.  $262^\circ$  (corr.; decomp.),  $[\alpha]_D - 26.05^\circ$  ( $\pm 0.6^\circ$ ).

d- $\alpha$ -Bromopropionyl-d-isoleucine,

$\text{CHMeBr} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$ , crystallises from water in branched needles, m. p.  $151$ — $152^\circ$  (corr.),  $[\alpha]_D^{20} + 24.5^\circ$  ( $\pm 0.4^\circ$ ).

d-Alanyl-d-isoleucine,  $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$ , crystallises from aqueous alcohol in drusy masses composed of needles, sinters at about  $220^\circ$ , has m. p.  $228$ — $229^\circ$  (corr.), and  $[\alpha]_D^{20} + 6.1^\circ$  ( $\pm 0.6^\circ$ ) in *N*-hydrochloric acid and  $-2.97^\circ$  ( $\pm 0.2^\circ$ ) in *N*-sodium hydroxide solution.

d-Alanyl-d-isoleucine anhydride, [3 : 6-diketo-2-methyl-5-sec.-butylpiperazine],  $\text{CHMe} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} \text{CH} \cdot \text{CHMeEt}$ , has m. p.  $250$ — $251^\circ$  (corr.; decomp.),  $[\alpha]_D^{20} - 16.6^\circ$  ( $\pm 0.1^\circ$ ).

d- $\alpha$ -Bromoisohexoyl-d-isoleucine,

$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$ , separates from aqueous alcohol in rhombic crystals, sinters at  $152^\circ$ , m. p.  $157$ — $158^\circ$ ,  $[\alpha]_D^{20} + 48.97^\circ$  ( $\pm 0.2^\circ$ ).

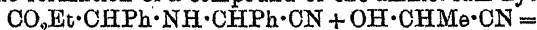
*l-Leucyl-d-isoleucine*,

$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CHMeEt}$ ,  
crystallises from aqueous alcohol in cubes, m. p.  $288^\circ$  (corr.),  
[ $\alpha$ ]<sub>D</sub><sup>20</sup> + 20.17° ( $\pm 0.2^\circ$ ) in *N*-hydrochloric acid; in *N*-sodium hydroxide  
solution it is feebly laevorotatory. T. H. P.

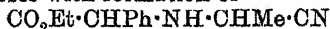
**The Degradation of Certain Di- and Hydroxy-amino-acids.**  
CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 20, 531—536).—*iso*Serine  
yields on oxidation with hydrogen peroxide in presence of ferrous  
sulphate, aminoacetaldehyde, from which a *p*-nitrophenylosazone was  
prepared, and also pyrazine, which is formed from it by oxidation with  
sodium hydroxide and mercuric chloride. Serine on oxidation under-  
goes deamination and yields glycol aldehydes.  $\alpha\beta$ -Diaminopropionic  
acid, on oxidation in similar circumstances, undergoes partial  
deamination only, the  $\beta$ -amino-group, as in *isoserine*, being stable,  
whereas the  $\alpha$ -group, as in serine, undergoes change. Aminoacet-  
aldehyde is, therefore, the chief oxidation product. *d*-Glucosamic acid  
yielded on oxidation a pentose. The course of oxidation of tyrosine  
under the same conditions is somewhat complicated. S. B. S.

**Esbach's Protein Estimation and a New Creatinine Com-  
pound.** ERNST MAYERHOFER (*Wien. Klin. Woch.*, 1909, 22, No. 3,  
Reprint).—When urine is boiled with 1% of picric acid and a strong  
mineral acid, there separates on cooling a crystalline *acid creatinine  
picrate*,  $\text{C}_4\text{H}_7\text{ON}_3 \cdot (\text{C}_6\text{H}_3\text{O}_7\text{N})_2$ , m. p.  $161$ — $166^\circ$ , which is formed  
by decomposition of Jaffé's double picrate of creatinine and potassium,  
into which it can be converted by potassium hydroxide. G. B.

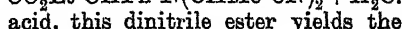
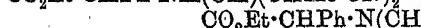
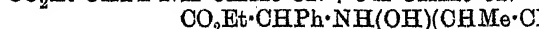
**Interaction of Derivatives of Iminodicarboxylic Acids and  
 $\alpha$ -Hydroxynitriles.** GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem.  
Soc.*, 1909, 41, 885—892. Compare Abstr., 1908, i, 251, 265; this  
vol., i, 106).—The interaction of the mixed nitrile and ethyl ester of  
*s*-di-*C*-phenyliminodiacetic acid with hydroxypropionitrile leads first to  
the formation of a compound of the ammonium hydroxide type,



$\text{CO}_2\text{Et} \cdot \text{CHPh} \cdot \text{NH}(\text{OH})(\text{CHPh} \cdot \text{CN})(\text{CHMe} \cdot \text{CN})$ ,  
which then decomposes with formation of

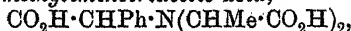


and  $\text{OH} \cdot \text{CHPh} \cdot \text{CN}$ . The nitrile ester of *s*-*C*-phenyl-*C*-methylimino-  
diacetic acid thus formed reacts with a fresh molecule of hydroxy-  
propionitrile, giving another ammonium hydroxide compound, which  
loses water and yields a dinitrile ester of a substituted iminotriacetic acid:



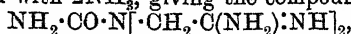
When heated with hydrochloric acid, this dinitrile ester yields the  
corresponding iminotriacetic acid.

*s*-*C*-Phenyl-di-*C*-methyliminotriacetic acid,



crystallises from water in silky needles, m. p.  $206$ — $208^\circ$ .

The author explains the formation of 4-iminohydantoin-1-acetamide by the action of alcoholic ammonia on carbomethoxyiminodiacetonitrile (compare Jongkees, Abstr., 1908, i, 959) as due to the replacement of the methoxy-group by an amino-group and union of the compound thus formed with  $2\text{NH}_3$ , giving the compound



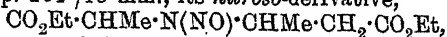
which, on boiling with water, loses ammonia, yielding 4-iminohydantoin-1-acetamide. An alternative explanation of the reaction is also given.

T. H. P.

**Iminodicarboxylic Acids.** GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 893—900).—Having shown that imino-acid derivatives of high molecular weight may be converted into similar derivatives of lower molecular weight, and that these are resolved into amino- and hydroxy-acids on hydrolysis (compare this vol., i, 106 and preceding abstract), the author has prepared the following new iminodicarboxylic acids and derivatives.

The hydrochloride of the nitrile ester of C-isobutyliminodiacetic acid,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CN}\cdot\text{HCl}$ , prepared from the ethyl ester of glycine and  $\gamma$ -methylpropaldehyde, has m. p.  $142^\circ$  (decomp.). The free nitrile ester,  $\text{C}_{16}\text{H}_{18}\text{O}_5\text{N}_2$ , is a colourless, mobile liquid, b. p.  $141\text{--}151^\circ/18$  mm., with a sweetish, stupefying odour. When boiled with dilute hydrochloric acid, the nitrile ester is converted into C-isobutyliminodiacetic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}_2\text{H}$ , which crystallises in thin needles, m. p.  $210\text{--}215^\circ$ . It forms a slightly soluble lead salt and an ethyl ester,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}_2\text{Et}$ , b. p.  $146^\circ/16$  mm., the nitroso-compound of which,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{N}(\text{NO})\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}_2\text{Et}$ , has b. p.  $179^\circ/17$  mm. and gives Liebermann's reaction.

*a*-Propio- $\beta$ -iminobutyric acid,  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared by the interaction of ethyl  $\beta$ -aminobutyrate hydrochloride, acetaldehyde, and potassium cyanide, forms slender, silky needles, m. p.  $216^\circ$  (decomp.), and is monobasic towards sodium hydroxide. The hydrochloride,  $\text{C}_{11}\text{H}_{14}\text{O}_4\text{NCl}$ , decomp.  $185\text{--}188^\circ$ ; ethyl ester,  $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}$ , b. p.  $131^\circ/15$  mm., its nitroso-derivative,



b. p.  $185^\circ/17$  mm., and the picrate, decomp.  $216^\circ$ , were prepared.

T. H. P.

**Action of Ammonia on Unsaturated Acids.** GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 900—908).—It was found by Eschweiler (Abstr., 1894, i, 267) that the result of the interaction of methylenecyanohydrin and ammonia depends on the active mass of the ammonia, and the author shows that, according to his explanation of the mechanism of the formation of derivatives of amino-, imino-, and nitrile acids (see preceding abstracts), the course of Eschweiler's reaction is in complete accord with Guldberg and Waage's law.

The author has studied the effect of the mass of the ammonia in the interaction of crotonic acid and ammonia by means of the following experiments: (1) 1 mol. crotonic acid and 4 mols. ammonia were heated in a sealed tube for twenty hours; of the crotonic acid which reacted

with the ammonia, 84.9% gave amino-acid and 15.1% imino-acid; (2) 1 mol. of crotonic acid and 2 mols. of ammonia were heated for ten hours; of the amount of crotonic acid reacting, 64% yielded amino-acid and 36% imino-acid. So that in the second case, despite the lessened duration of heating, the proportion of imino-acid obtained is considerably greater than in the first experiment.

*Diethyl di-C-methyliminodipropionate*,  $\text{NH}(\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , prepared from the corresponding ammonium salt yielded by the action of ammonia on crotonic acid, is a colourless liquid, b. p.  $150\text{--}150.5^\circ/15$  mm. The copper salt,  $\text{C}_8\text{H}_{15}\text{O}_4\text{NCu}$ , was analysed, but the following compounds could not be obtained crystalline: the free acid, which has an acid reaction with litmus, the amide, which is intensely alkaline towards litmus, and the hydrochloride.

When heated in a sealed tube, fumaric acid (1 mol.) and aqueous ammonia (3 mols.) (compare Körner and Menozzi, Abstr., 1890, 869) yield aspartic acid and iminodisuccinic acid, the *tetraethyl* ester of which,  $\text{NH}[\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}]_2$ , is an extremely viscous liquid, b. p.  $215\text{--}217^\circ/15$  mm. T. H. P.

**Action of Ammonia on the Homologues of Acetone.** WILHELM TRAUBE (*Ber.*, 1909, 42, 3298—3304).—Contrary to the statements of Thomae (compare Abstr., 1905, i, 509; 1907, i, 113), methyl ethyl ketone and methyl propyl ketone behave like acetone towards ammonia.

It is found that the action of ammonia on methyl ethyl ketone leads, not only to the formation of 2:3:6-trimethyl-2:6-diethyl-4-piperidone (compare Abstr., 1908, i, 363), but also of *dimethyldiacetoneamine*,  $\text{COEt}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{NH}_2$  or  $\text{COMe}\cdot\text{CHMe}\cdot\text{CMeEt}\cdot\text{NH}_2$ , obtained as a basic oil which could not be purified, since it decomposes when distilled under greatly diminished pressure and does not form crystalline salts; it liberates ammonia when boiled, and yields *dimethylmesityl oxide*,  $\text{COEt}\cdot\text{CH}\cdot\text{CMeEt}$  or  $\text{COMe}\cdot\text{CMe}\cdot\text{CMeEt}$ , probably identical with the compound obtained by Schramm by the action of sodium on methyl ethyl ketone (compare Abstr., 1883, 1079).

*Diethyldiacetoneamine*,  $\text{COPr}^a\cdot\text{CH}_2\cdot\text{CMePr}^a\cdot\text{NH}_2$  or  $\text{COMe}\cdot\text{CHEt}\cdot\text{CMePr}^a\cdot\text{NH}_2$ ,

appears to be the only base formed by the action of ammonia on methyl propyl ketone; it is an oil, b. p.  $146^\circ/16$  mm. (slight decomp.), which when boiled under atmospheric pressure decomposes into ammonia and *diethylmesityl oxide*,  $\text{C}_{10}\text{H}_{18}\text{O}$ , a pale yellow liquid with an unpleasant odour, b. p.  $198\text{--}199^\circ/760$  mm. Diethyldiacetoneamine when reduced with sodium amalgam and dilute acid yields the corresponding *alkamine*, which, however, could not be obtained in a pure state. W. H. G.

**Rearrangements.** GEORG SCHROETER (*Ber.*, 1909, 42, 3356—3362).—In preparing carbimides from azoimides (compare this vol., i, 617) it is not necessary, as a rule, to isolate the latter, but it is often sufficient to heat the acid chloride with commercial sodium azoimide in a suitable indifferent solvent until the evolution of

nitrogen is at an end. In this way the following carbimides have been prepared: (1) methylcarbimide; (2) *chloromethylcarbimide*,  $\text{CH}_2\text{Cl}\cdot\text{N}\cdot\text{CO}$ , b. p. 80—81°; with trichloroacetyl chloride and sodium azoimide, the evolution of nitrogen is incomplete, even after prolonged heating at a high temperature; (3) *n*-hexylcarbimide; (4) *n*-heptadecylcarbimide,  $\text{C}_{17}\text{H}_{35}\cdot\text{N}\cdot\text{CO}$ , b. p. 208—209°/17 mm.; (5) phenylcarbimide.

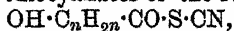
[With MOTSCHMANN.]—The constitution of 1:5-diphenyl-1:2:3:4-tetrazole (*loc. cit.*) is confirmed by the synthesis of this compound from benzenyliminophenyl chloride and sodium azoimide. In preparing 1:5-diphenyl-1:2:3:4-tetrazole from benzophenone chloride, it is not necessary to treat the chloride with silver azoimide, since sodium azoimide in amyl ether gives the same result.

The formation of diphenylketen from azibenzil (benzoylphenylazomethylene) (*loc. cit.*) is a result of the rearrangement of the grouping  $\text{CPhBz}$ . The velocity of this rearrangement is studied by observing the transformation of azibenzil with alcohols (*loc. cit.*), in which about 70% of diphenylacetic ester and 30% of benzoin ether are formed. Hence at the temperature employed (40—60°) the grouping  $\text{CPhBz}$  is transformed into diphenylketen with measurable velocity, so that a part of the alcohol has time to occupy the free valencies of the phenylbenzoylmethylene.

T. H. P.

**Ureides and Cyanamides of the Hydroxy-fatty Acids. II.** ERIK CLEMMENSEN and ARNOLD H. C. HEITMAN (*Amer. Chem. J.*, 1909, 42, 319—340).—In an earlier paper (*Abstr.*, 1908, i, 771) it has been shown that when the esters of the dialkylglycollic acids are treated with carbamide in presence of sodium ethoxide, ureides of the formula  $\text{OH}\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CR}_2\cdot\text{OH}$  are formed, whilst if thiocarbamide or guanidine is used instead of carbamide, dialkylglycollylcyanamides are produced.

The investigation has now been extended to glycollic, lactic,  $\alpha$ -hydroxybutyric, and  $\alpha$ -hydroxyisovaleric acids, and these have been found to behave in a similar manner. The ureides so obtained have low m. p.'s, and act as rather strong dibasic acids. The cyanamides are well-crystallised substances of high melting point, which, when boiled with dilute acids, are converted quantitatively into the corresponding ureides. The mother liquors from the cyanamides contain small quantities of acyl thiocyanates of the formula



these being the first acyl thiocyanates yet obtained (compare Dixon, *Trans.*, 1908, 93, 699); these compounds are stable, crystalline substances, and can be boiled with water or dilute acids without decomposition.

In preparing the esters of the  $\alpha$ -hydroxy-fatty acids, it has been found that good yields can be obtained by heating the respective acids with excess of alcohol in presence of copper sulphate which has been dehydrated at a low temperature in order to obviate the formation of any sulphuric anhydride.

*Diglycollylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH})_2$ , m. p. 88—89°, forms thin, colourless plates, and is not changed when boiled with solutions

of carbonates or dilute acids, but is decomposed by dilute alkali hydroxides with evolution of ammonia. The *silver* salt forms long, monoclinic prisms containing 2.5 mols.  $\text{H}_2\text{O}$ .

*Dilactylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OH})_2$ , m. p. 49—50°, crystallises in small needles, and behaves towards alkalis in the same way as diglycollylcarbamide. On adding copper chloride to excess of concentrated solutions of calcium, barium, strontium, or magnesium salts of the carbamide, double salts of the formula  $\text{C}_{14}\text{H}_{20}\text{O}_{10}\text{N}_4\text{CuM}$  are obtained as blue precipitates. The *silver* salt crystallises in small needles containing 1.5 mols.  $\text{H}_2\text{O}$ .

*Di- $\alpha$ -hydroxybutyrylcarbamide*,  $\text{CO}[\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Me}]_2$ , m. p. 48—49°, forms short, prismatic crystals and yields blue double salts of the formula  $\text{C}_{18}\text{H}_{28}\text{O}_{10}\text{N}_4\text{CuM}$  (where M is Ca, Ba, Sr, or Mg). The *silver* salt forms small, monoclinic needles containing 1.5 mols.  $\text{H}_2\text{O}$ .

*Di- $\alpha$ -hydroxyisovalerylcarbamide*,  $\text{CO}[\text{NH}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2]_2$ , b. p. 277—279°/760 mm., forms a colourless oil, has  $D^{15}_D$  1.1922, and gives double salts of the formula  $\text{C}_{22}\text{H}_{36}\text{O}_{10}\text{N}_4\text{CuM}$  (where M is Ca, Ba, Sr, or Mg). The *silver* salt forms slender, monoclinic needles containing 2.5 mols.  $\text{H}_2\text{O}$ .

*Glycollycyanamide*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$ , m. p. 217—237° (decomp.), forms large, lustrous, monoclinic prisms.

*Glycollythiocyanate*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{S}\cdot\text{CN}$ , m. p. 106°, crystallises in slender, yellow needles.

*Lactylcyanamide* (Merting, *J. pr. Chem.*, 1878, [ii], 7, 31) softens at 208° and melts at 212°.

*Lactyl thiocyanate*,  $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{S}\cdot\text{CN}$ , m. p. 89—90°, forms small, colourless needles.

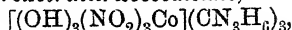
*$\alpha$ -Hydroxybutyrylcyanamide*,  $\text{CH}_2\text{Me}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$ , m. p. 207—208°, forms thin, lustrous plates or silky needles.

*$\alpha$ -Hydroxyisovalerylcyanamide*,  $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$ , crystallises in needles, softens at 216°, and melts at 219°. E. G.

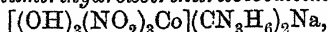
**Carbonyldicarbamide as an Oxidation Product of Uric Acid.** ALFRED SCHITTENHELM and KARL WIENER (*Zeitsch. physiol. Chem.*, 1909, 62, 100—106).—Scholz has already shown that by oxidising uric acid with hydrogen peroxide in alkaline solution, tetracarbonimide is obtained. A further oxidation product, carbonyldicarbamide, can be obtained by slightly varying the conditions employed by Scholz, in that the oxidation mixture is warmed from half to one hour on a water-bath. Oxalic acid was also obtained, and a substance which gives a derivative with  $\alpha$ -naphthalenesulphonyl chloride.

S. B. S.

**Action of Guanidine Carbonate on Sodium Cobaltinitrite: Trihydroxotritritocobaltate.** KARL A. HOFMANN and KARL BUCHNER (*Ber.*, 1909, 42, 3389—3392).—Guanidine carbonate acts on cobaltinitrites as though it were the carbonate of a mono-acid guanidinium base (compare Grossmann and Schück, *Abstr.*, 1907, i, 142), nitrito-groups being replaced by hydroxyl groups with formation of salts,  $[(\text{OH})_3(\text{NO}_2)_3\text{Co}](\text{CN}_3\text{H}_6)_3$  and  $[(\text{OH})_3(\text{NO}_2)_3\text{Co}](\text{CN}_3\text{H}_6)_2\text{Na}$ , of one of the hydroxonitrito-acids,  $[(\text{OH})_n(\text{NO}_2)_{6-n}\text{Co}]\text{H}_3$ , intermediate to the nitritocobalti-acids and cobaltihydroxide.

*Guanidiniumtrihydroxotritritocobaltiate*,

crystallises in garnet-red, rhombic prisms, and is decomposed by water, rapidly on heating, into cobaltihydroxide and nitrite; the molecular weight in water, determined cryoscopically, is at first normal, but soon falls to the value, 151, indicated by this decomposition.

*Sodium guanidiniumtrihydroxotritritocobaltiate*,

forms garnet-red crystals belonging to the rhombic system [STEINMETZ:  $a:b:c=0.3775:1:0.32$ ], and is decomposed by water. The corresponding *silver* salt,  $\text{C}_2\text{H}_{15}\text{O}_9\text{N}_9\text{AgCo}$ , separates in reddish-brown, shining leaflets, is decomposed by water, and gives silver chloride or chromate when treated with potassium chloride or dichromate.

T. H. P.

**Polymerisation of Fulminic Acid.** F. CARLO PALAZZO (*Gazzetta*, 1909, 39, ii, 249—267. Compare Abstr., 1907, i, 298, 489).—The views of Wieland and Hess (this vol., i, 369) are criticised.

T. H. P.

**Perthiocyanic Acid and Trithioallophanic Acid.** ARTHUR ROSENHEIM, RICHARD LEVY, and HERBERT GRÜNBAUM (*Ber.*, 1909, 42, 2923—2929. Compare Hantzsch and Wolvekamp, Abstr., 1904, i, 718).—The formula  $\begin{array}{c} \text{S} \\ | \\ \text{CS}\cdot\text{NH} \end{array} \text{---} \text{S} \text{---} \text{C}\cdot\text{NH}$  for xanthanic acid, proposed by

Hantzsch and Wolvekamp, is supported by the following observations.

The ester of cyanamidodithiocarbonate undergoes rearrangement in aqueous solution containing hydrochloric acid into the ester of carbamidodithiocarbonate,  $\text{O}(\text{SR})_2\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$ . By the action of hydrogen sulphide on potassium cyanamidodithiocarbonate, reduction takes place as well as the addition of hydrogen sulphide, and *potassium trithioallophanate* is formed,  $\text{S}\cdot\text{C}(\text{KS})\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ . This compound reacts with benzyl chloride, forming the benzyl trithioallophanate previously prepared by Fromm and Göncz (Abstr., 1907, i, 872).

*Potassium trithioallophanate* forms light yellow, lustrous crystals; the *copper* salt forms a characteristic amorphous, reddish-brown precipitate; the *silver* salt is bright red; the *lead* salt orange-red. The *methyl* ester forms yellowish-white crystals, m. p.  $164^\circ$ ; the *ethyl* ester has m. p.  $174^\circ$ .

*Potassium trithioallophanate* is also obtained by the direct action of hydrogen sulphide on molecular quantities of carbon disulphide and thiocarbamide in alkaline alcoholic solution. It is identical with the salt described by Klason as acid potassium perthiocyanate, but not obtained by him in the crystalline state.

Benzyltrithioallophanic acid forms bright yellow needles, m. p.  $144^\circ$  (Fromm, *loc. cit.*). *Benzyl perthiocyanate* forms colourless plates, m. p.  $52^\circ$ .

E. F. A.

**Production of Hydrocyanic Acid from Ammonia and Wood. Charcoal, and also from Di- and Tri-methylamine** G. A. VOERKELIUS (*Chem. Zeit.*, 1909, 33, 1025—1026, 1078—1081, 1090—1092).—In Dessau, Bueb's process (*Zeitsch. angew. Chem.*, 1906,

19, 609) for making cyanides from the organic compounds contained in beet molasses is worked. The molasses are first submitted to destructive distillation at  $600^{\circ}$ . The gases evolved contain water vapour, carbon monoxide and dioxide, hydrogen, methane, nitrogen, ammonia, and methylamine; they are heated to  $800$ — $1000^{\circ}$  and then contain about 7% of hydrogen cyanide, the methylamine having disappeared. The present paper gives an account of experiments which have been made with the object of throwing light on the reactions which occur in the superheater. Mixtures of hydrogen and either ammonia, di- or tri-methylamine were passed through a tube heated to a definite temperature and filled with material which varied in different experiments. The products of reaction were analysed, and conclusions as to the course of the reactions could be drawn from the results.

When a mixture of ammonia and hydrogen is led over wood charcoal at temperatures higher than  $700^{\circ}$ , hydrogen cyanide and nitrogen are produced, but no methane. Some ammonia and hydrogen remain undecomposed. The proportion of ammonia to hydrogen cyanide varies, so that pure ammonium cyanide is not produced. The yields of hydrogen cyanide and undecomposed ammonia increase with increasing dilution of the ammonia by hydrogen, and also with the rate of flow of gases through the tube. The best yield is obtained at about  $1000^{\circ}$ . Dilution with coal-gas gives a better yield of hydrogen cyanide than when hydrogen is used as the diluent. The reactivity of the wood charcoal diminishes with continued use. The hydrogen cyanide is formed according to the reversible equation:  $\text{NH}_3 + \text{C} \rightleftharpoons \text{HCN} + \text{H}_2$ . At the same time the reversible reactions  $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$  and  $2\text{HCN} \rightleftharpoons \text{N}_2 + \text{H}_2 + 2\text{C}$  also play a part. The two latter reactions are catalytically affected by the material contained in the tube, as was shown by experiments with wood charcoal, chamotte, and a material known as "Marquardt's mass." Glazed material is not nearly so catalytically active as porous material.

At  $800$ — $1000^{\circ}$  trimethylamine is decomposed to the extent of about 98% into hydrogen cyanide and methane, according to the equation  $\text{N}(\text{CH}_3)_3 = \text{HCN} + 2\text{CH}_4$ . The concentration of the mixed gases—hydrogen and trimethylamine—has no influence on the result, nor has the velocity of flow through the tube much effect. Increasing the velocity slightly increases the yield. If contact substances are avoided and the velocity of flow is not too small, all the hydrogen cyanide produced according to the above equation can be obtained, since even at  $1000^{\circ}$  the velocity of decomposition of hydrogen cyanide is very small. Raising the temperature above  $1000^{\circ}$  or allowing the hot gases to come into contact with iron, chamotte, or other porous material, decomposes part of the hydrogen cyanide. Between  $800$  and  $1000^{\circ}$  about 2% of the trimethylamine decomposes according to the equation:  $\text{N}(\text{CH}_3)_3 + 3\text{H}_2 = \text{NH}_3 + 3\text{CH}_4$ . At  $720^{\circ}$  only 78% of hydrogen cyanide is produced. At  $600^{\circ}$  no cyanide is formed, but only a base, which is probably tetramethylhydrazine.

At  $820$ — $1120^{\circ}$  dimethylamine decomposes quantitatively according to the equation:  $\text{NH}(\text{CH}_3)_2 = \text{HCN} + \text{CH}_4 + \text{H}_2$ . If the dimethylamine is diluted with more than 50% of hydrogen, a part of it is decomposed according to the equation:  $\text{NH}(\text{CH}_3)_2 + 2\text{H}_2 = \text{NH}_3 +$

$2\text{CH}_4$ . As the percentage of hydrogen increases, the reaction proceeds more and more according to the second equation, until with 97% of hydrogen no hydrogen cyanide is formed, but only ammonia. At  $620^\circ$  no hydrogen cyanide is formed, and at  $720^\circ$  a smaller amount than at higher temperatures.

T. S. P.

Nitro-derivatives of 3:5-Dibromotoluene. JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 728—730. Compare Nevile and Winther, *Trans.*, 1881, 39, 83; Blanksma, *Abstr.*, 1904, i, 566; 1905, i, 761).

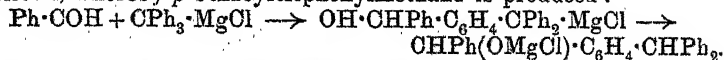
—Nitro-derivatives of 3:5-dibromotoluene have been prepared. Diazotisation of 3:5-dibromo-4-nitro-*o*-toluidine yields two products: 3:5-dibromo-4-nitrotoluene, colourless crystals (from light petroleum), m. p.  $84^\circ$ , and converted by nitric acid into Nevile and Winther's 3:5-dibromo-2:4-dinitrotoluene; and a *by-product*, m. p. about  $250^\circ$ , much less soluble in alcohol than the other product of the reaction. A mixture of concentrated nitric and sulphuric acids converts both 3:5-dibromo-4-nitrotoluene and 3:5-dibromo-2:4-dinitrotoluene into 3:5-dibromo-2:4:6-trinitrotoluene.

Diazotisation of 3:5-dibromo-2-nitro-*p*-toluidine produces 3:5-dibromo-2-nitrotoluene, which is separated from a *by-product* of higher melting point by solution in alcohol and crystallisation from light petroleum. Thus purified, it has m. p.  $67^\circ$ . Nitric acid (D 1.52) converts it into a mixture of 3:5-dibromo-2:4-dinitrotoluene and 3:5-dibromo-2:6-dinitrotoluene, the latter not being obtained free from the former, but a mixture of nitric acid and sulphuric acid yields 3:5-dibromo-2:4:6-trinitrotoluene. 3:5-Dibromo-2:6-dinitrotoluene can be prepared by diazotising 3:5-dibromo-2:6-dinitro-*p*-toluidine, extracting with alcohol, and recrystallising from light petroleum. It has m. p.  $117^\circ$ .

On crystallisation from alcohol, a mixture of 3:5-dibromo-2:4-dinitrotoluene and 3:5-dibromo-2:6-dinitrotoluene forms crystals, m. p.  $106\text{--}108^\circ$ , previously prepared by Nevile and Winther, and identified as mixed crystals by the author. All the possible mono-, di-, and tri-nitro-derivatives of 3:5-dibromotoluene have been prepared.

A. J. W.

Existence of Two Isomeric Magnesium Triphenylmethyl Chlorides. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1909, 42, 3469—3479). —Of the three reactions quoted by Schmidlin for the differentiation of his  $\alpha$ - and  $\beta$ -modifications of magnesium triphenylmethyl chloride (*Abstr.*, 1907, i, 26), the reactions with water and with carbon dioxide have been proved fallacious (Tschitschibabin, *ibid.*, i, 1022). Only the reaction with benzaldehyde remains, and the author now shows that this can be explained without the assumption of the existence of two modifications of magnesium triphenylmethyl chloride. He has already suggested (*loc. cit.*) that this substance may react with benzaldehyde normally, yielding  $\beta$ -benzopinacolin, and also abnormally as follows, whereby *p*-benzoyltriphenylmethane is produced:



Illustrations of such abnormal condensation are found in the reaction between formaldehyde and magnesium benzyl chloride, whereby both

benzylcarbinol and *o*-tolylcarbinol are formed (Tiffeneau and Delange, *Abstr.*, 1904, i, 48), and also in the reaction between benzaldehyde and magnesium benzyl chloride, which leads to the formation of phenylbenzylcarbinol, phenyl-*o*-tolylcarbinol, and phenyl-*p*-tolylcarbinol.

The author has also obtained both benzopinacolin and *p*-benzoyltriphenylmethane from solutions of magnesium triphenylmethyl chloride, which should contain, according to Schmidlin, only the  $\beta$ -modification, and also from solutions which should contain only the  $\alpha$ -form. Hence he draws the conclusion that there is no evidence for the existence of two isomeric magnesium triphenylmethyl chlorides.

C. S.

**Phenanthrene-3-sulphonic Acid and Certain of its Derivatives.** HÅKAN SANDQVIST (*Annalen*, 1909, 369, 104—117. Compare Werner, *Abstr.*, 1902, i, 437).—Phenanthrene-3-sulphonic acid crystallises in white leaflets and retains  $1\text{H}_2\text{O}$  at 60–65°; this hydrate has m. p. 120–121°, and yields the anhydrous acid, m. p. 175–177°, when heated above 86°; the latter substance absorbs  $2\text{H}_2\text{O}$  from the air and then has m. p. 88–89°. The mol. conductivities at 18° of aqueous solutions  $v = 32, 64, 128, 256, 512, \text{ and } 1024$  were found to be 313.2, 319.3, 325.2, 328.2, 330.4, and 335.5 respectively. The acid does not follow Ostwald's dilution law, or yet agree with the empirical formulæ of van't Hoff and Rudolphi.

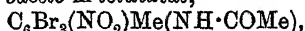
The following salts were analysed and their solubilities determined; the value recorded is the weight of anhydrous salt in grams which will dissolve in 100 grams of water at 20°: *potassium*, sol. = 0.342; *ammonium*, white leaflets, sol. = 0.26; *sodium* ( $1\text{H}_2\text{O}$ ), irregular, granular crystals, sol. = 1.1; *calcium* ( $2\text{H}_2\text{O}$ ), faintly yellowish-brown, granular crystals, sol. = 0.11; *barium* ( $3\text{H}_2\text{O}$ ), white leaflets, sol. = 0.03; *magnesium* ( $4\text{H}_2\text{O}$ ), large, slender, faintly yellowish-brown leaflets, sol. = 0.116; *zinc* ( $4\text{H}_2\text{O}$ ), pale yellow, crystalline powder, sol. = 0.19; *ferrous* ( $5\text{H}_2\text{O}$ ), slightly yellow, crystalline powder, sol. = 0.2; *lead* ( $3\text{H}_2\text{O}$ ), slightly yellowish-brown, crystalline mass, sol. = 0.08; *copper* ( $4\text{H}_2\text{O}$ ), pale green spangles, sol. = 0.09; *silver*, white leaflets, sol. = 0.20.

Phenanthrene-3-sulphonyl chloride has m. p. 110–111°, sometimes 114°; when treated with ethyl alcohol, it yields the corresponding *ethyl ester*,  $\text{C}_{14}\text{H}_9\cdot\text{SO}_2\cdot\text{OEt}$ , which crystallises in elongated leaflets and needles, m. p. 107–108°; the *sulphonyl bromide*,  $\text{C}_{14}\text{H}_9\cdot\text{SO}_2\text{Br}$ , crystallises in pale yellow, transparent, cubical and rhomboidal plates, m. p. 140°; the *sulphonamide*,  $\text{C}_{14}\text{H}_9\cdot\text{SO}_2\cdot\text{NH}_2$ , forms colourless leaflets, m. p. 189.5–190°. The sulphonyl chloride when heated with phosphorus pentachloride yields 3-*chlorophenanthrene*,  $\text{C}_{14}\text{H}_9\text{Cl}$ , aggregates of needles, m. p. 81° and 70.5–71°, and a *dichlorophenanthrene*,  $\text{C}_{14}\text{H}_8\text{Cl}_2$ , white crystals, m. p. 124°. W. H. G.

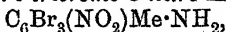
**Acetylation with Acetic Anhydride and Sulphuric Acid.** JAN J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 717–727).—A number of acetyl derivatives have been prepared by acetylation with acetic anhydride and a drop of concentrated sulphuric acid. For the mono-

acetyl derivatives the reaction was moderated by dissolving the substance in about ten times its weight of glacial acetic acid. The mono- and di-acetyl derivatives of the following have been prepared: 3:5-dibromo-*o*-toluidine, 3:5-dibromo-*p*-toluidine, 2:6-dichloro-4-nitroaniline, 2:6-dibromo-4-nitroaniline, 4:6-dibromo-2-nitroaniline, 2:4:6-tribromo-3-nitroaniline, and *o*-, *m*-, and *p*-nitroanilines. The monoacetyl derivatives of 2:3-, 2:4-, 2:5-, 3:4-, and 3:5-dinitroaniline have been prepared. *o*-Nitrodiaacetanilide forms colourless crystals, m. p. 94°. The diacetyl derivative of 2:4:6-trinitro-*m*-phenylenediamine,  $C_6H(NO_2)_3(NH \cdot COMe)_2$ , is colourless, does not melt below 300°, but darkens in colour at this temperature. 2:4:6-Tribromoaceto-*m*-toluidide forms colourless crystals, m. p. 205°. 2:4:6-Tribromodiaceto-*m*-toluidide (colourless crystals) has m. p. 103°.

Nitric acid (D 1.52) converts 2:4:6-tribromoaceto-*m*-toluidide into 2:4:6-tribromo-5-nitroaceto-*m*-toluidide,



colourless needles, m. p. 261°, which, with concentrated sulphuric acid at 110°, yields 2:4:6-tribromo-5-nitro-*m*-toluidine,

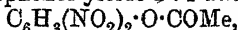


pale yellow needles, m. p. 184°.

2:4:6-Tribromo-5-nitrodiaaceto-*m*-toluidide forms colourless crystals (from alcohol), m. p. 188°. *s*-2:4:6-Tribromoaceto-*xy*lidide forms colourless crystals, m. p. 258°. 2:4:6-Tribromo-3:5-dinitroaceto-*anilide* has m. p. 275°, and the corresponding diacetyl derivative has m. p. 165°.

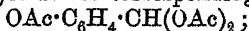
Bromine converts 4-nitro-*o*-toluidine into 3:5-dibromo-4-nitro-*o*-toluidine,  $C_6HBr_2(NO_2)Me \cdot NH_2$ , yellow crystals, m. p. 104° which yields 3:5-dibromo-4-nitroaceto-*o*-toluidide (colourless crystals, m. p. 201°) and 3:5-dibromo-4-nitrodiaaceto-*o*-toluidide, m. p. 159°. With nitric acid (D 1.52) and concentrated sulphuric acid, 3:5-dibromo-4-nitroaceto-*o*-toluidide yields 3:5-dibromo-4:6-dinitroacetotoluidide, white crystals, m. p. 280°. Bromination converts 2-nitro-*p*-toluidine into 3:5-dibromo-2-nitro-*p*-toluidine, yellow crystals, m. p. 82°, which yields 3:5-dibromo-2-nitroaceto-*p*-toluidide (compare Kunckell, this vol., i, 20).

The acetyl derivatives of *o*- and *p*-nitrophenol, 2:4:6-trinitrophenol, 2:4:6-tribromophenol, and 2:6-dibromo-4-nitrophenol have also been prepared. 2:4-Dinitrophenol yields 2:4-dinitrophenyl acetate,



colourless crystals, m. p. 72°. 2:4-Dibromo-6-nitrophenol yields 2:4-dibromo-6-nitrophenyl acetate,  $C_6H_2Br_2(NO_2) \cdot O \cdot COMe$ , colourless crystals, m. p. 88°.

Benzaldehyde yields benzylidene diacetate,  $C_6H_5 \cdot CH(OAc)_2$ ; *p*-hydroxybenzaldehyde yields the corresponding triacetate,

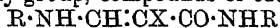


furfuraldehyde yields furfurylidene diacetate,  $C_4H_3O \cdot CH(OAc)_2$ , which has m. p. 52° (from light petroleum). Law (Abstr., 1908, i, 321) gives 45°, but he employed alcohol, which is an unsatisfactory solvent for this compound. Methylfurfuraldehyde yields 2-methylfurfurylidene diacetate,  $C_4H_2OMe \cdot CH(OAc)_2$ , colourless crystals, m. p. 95°. 4-Hydroxy-2-methylfurfuraldehyde yields the corresponding triacetyl

derivative,  $\text{OAc}\cdot\text{C}_6\text{OHMe}\cdot\text{CH}(\text{OAc})_2$ , colourless crystals from light petroleum, m. p.  $73^\circ$ .

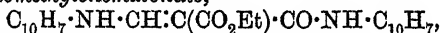
The process furnishes a rapid acetylation method for aldehydes, and for derivatives of aniline and phenol. A. J. W.

**Reactions of the Formamidine Derivatives.** FRANK B. DAINS and E. W. BROWN (*J. Amer. Chem. Soc.*, 1909, 31, 1148—1157).—It has been shown previously (Abstr., 1902, i, 692) that the disubstituted formamidines react with compounds containing a methylene group to form compounds of the type  $\text{R}\cdot\text{NH}\cdot\text{CH}\cdot\text{CXY}$ , and that when Y represents a carbethoxy-group, compounds of the type



are obtained. The completeness of the latter reaction depends on the temperature and the nature of the compound containing the methylene group. Thus with ethyl malonate, a quantitative yield of amide is produced; with ethyl acetoacetate, 50—80% of the amine reacts with the carbethoxy-group, whilst with ethyl cyanoacetate no amide is formed. The former reaction, namely, the replacement of the hydrogen atoms of the methylene group by  $\cdot\text{CH}\cdot\text{NHR}$ , seems to be affected by the positive or negative nature of the molecule. Thus benzyl cyanide and deoxybenzoin react with greater difficulty than the more negative ethyl malonate or acetoacetate, and the more positive methylpyrazolone fails to combine with diphenylformamidine, whilst phenylmethyl- and diphenylpyrazolone unite with it readily.

The following compounds have been obtained by the reaction of formamidines with ethyl malonate. The  $\alpha$ -naphthylamide of ethyl  $\alpha$ -naphthylaminomethylenemalonate,



m. p.  $162^\circ$ , yields a bromo-derivative, m. p.  $227^\circ$ . The corresponding  $\beta$ -naphthyl compound melts at  $172^\circ$ . When malonanilide is heated with di- $\beta$ -naphthylformamidine,  $\beta$ -naphthylamine and  $\beta$ -naphthylaminomethylenemalonanilide,  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CH}\cdot\text{C}(\text{CO}\cdot\text{NHPH})_2$ , m. p.  $289^\circ$ , are produced. The *m*-toluidide of ethyl *m*-toluidinomethylenemalonate melts at  $95^\circ$ . Methylenedi-*o*-phenetidins, m. p.  $81^\circ$ , obtained by heating ethyl orthoformate with *o*-phenetidine at  $140^\circ$ , yields a platini-chloride, m. p.  $178^\circ$ , and reacts with ethyl malonate, with formation of the *o*-phenetidide of ethyl *o*-phenetidinomethylenemalonate, m. p.  $110^\circ$ .

With ethyl acetoacetate, the following compounds were obtained: *p*-Bromoacetoacetylanilide, m. p.  $137.5^\circ$ , was prepared by the action of *p*-bromoaniline. Anilinomethyleneacetoacetyl-*p*-bromoanilide and the isomeric *p*-bromoanilinomethyleneacetoacetanilide melt at  $158^\circ$  and  $171^\circ$  respectively. Di-*p*-bromophenylformamidine, m. p.  $170^\circ$ , reacts with ethyl acetoacetate to form *p*-bromoanilinomethyleneacetoacetyl-*p*-bromoanilide, m. p.  $190^\circ$ , together with ethyl *p*-bromoanilinomethyleneacetoacetate, m. p.  $107^\circ$ . *p*-Toluidinomethyleneacetoacetanilide melts at  $142^\circ$ .  $\psi$ -Cumidinomethyleneacetoacetyl- $\psi$ -cumidide and ethyl  $\psi$ -cumidinomethyleneacetoacetate melt at  $183^\circ$  and  $98^\circ$  respectively. Ethyl *o*-anisidinomethyleneacetoacetate melts at  $112^\circ$ , at  $138^\circ$  *p*-phenetidinomethyleneacetoacetyl-*p*-phenetidide at  $138^\circ$ .  $\alpha$ -Naphthylaminomethyleneacetoacetyl- $\alpha$ -naphthylamide, m. p.  $167$ — $168^\circ$ , yields a dibromide, m. p.  $226^\circ$ . Ethyl  $\alpha$ -naphthylaminomethyleneacetoacetate melts at  $92^\circ$ .  $\beta$ -Naphthyl-

aminomethyleneacetacetyl- $\beta$ -naphthylamide and ethyl  $\beta$ -naphthylaminomethyleneacetate melt at 184° and 95° respectively.

The following compounds of ethyl cyanoacetate are described: Ethyl  $\psi$ -cumidinomethyleneacyanoacetate, m. p. 196°, ethyl  $\alpha$ -naphthylaminomethyleneacyanoacetate, m. p. 146°, and ethyl  $\beta$ -naphthylaminomethyleneacyanoacetate, m. p. 152°.

With phenylacetoneitrile there were obtained *m*-toluidinomethylenebenzyl cyanide, m. p. 126°, and  $\beta$ -naphthylaminomethylenebenzyl cyanide, m. p. 194°.

Deoxybenzoin unites with di- $\alpha$ -naphthylformamidine to form  $\alpha$ -naphthylaminomethylenedeoxybenzoin, m. p. 161°.

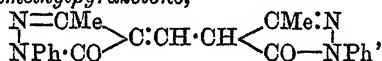
The following compounds were obtained with acetylacetone: *o*-toluidinomethyleneacetylacetone, m. p. 124°, the corresponding *m*-toluidino-derivative, m. p. 75°, *o*-phenetidinomethyleneacetylacetone, m. p. 115—116°, and  $\alpha$ - and  $\beta$ -naphthylaminomethyleneacetylacetone, melting at 144° and 129° respectively.

Phenylmethylpyrazolone and the formamidines react smoothly in accordance with the equation:

$$\begin{array}{c} \text{N}=\text{CMe} \\ | \\ \text{NPh}\cdot\text{CO} \end{array} \text{CH}_2 + \text{NR}\cdot\text{CH}\cdot\text{NHR} \rightarrow \begin{array}{c} \text{N}=\text{CMe} \\ | \\ \text{NPh}\cdot\text{CO} \end{array} \text{C}\cdot\text{CH}\cdot\text{NHR},$$

yielding red or yellow substituted aminoethylenepyrazolones.

Methylenebisphenylmethylpyrazolone,



m. p. 180°, is sometimes formed in this reaction, this being the first instance in which both the NR· and NHR· groups of the substituted formamidines have been replaced in reactions with methylene derivatives. The following compounds are described: 4-Anilinomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 154°, 4- $\beta$ -naphthylaminomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 177°, the corresponding  $\alpha$ -naphthyl derivative, m. p. 122°, 4-*p*-bromoanilinomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 168°, 4-*p*-toluidinomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 164°, 4- $\psi$ -cumidinomethylene-1-phenyl-3-methyl-5-pyrazolone, m. p. 171°, 4-*p*-phenetidinomethylene-1-phenyl-3-methyl-5-pyrazolone, 4-anilinomethylene-1:3-diphenyl-5-pyrazolone, m. p. 140°, 4-*o*-toluidinomethylene-1:3-diphenyl-5-pyrazolone, m. p. 146°, and 4- $\beta$ -naphthylaminomethylene-1:3-diphenyl-5-pyrazolone, m. p. 192°.

By the action of phenylhydrazine on anilinomethylenebenzoylacetanilide and *o*-toluidinomethylenebenzoylaceto-*o*-toluidide, Rüggeberg (*Diss.*, 1904) obtained compounds, m. p. 155° and 160°, which he regarded as aminomethylene derivatives of diphenylpyrazolone, but which do not appear identical with the anilinomethylene- and *o*-toluidinomethylene-diphenylpyrazolones described previously, which melt at 140° and 146° respectively. On repeating the work with *o*-toluidinomethylenebenzoylaceto-*o*-toluidide, it has been found that the compound obtained by Rüggeberg is the *o*-toluidide of 5-diphenylpyrazolecarboxylic acid, m. p. 165°. When ethyl  $\beta$ -naphthylaminomethyleneacetate is boiled with phenylhydrazine, ethyl 1-phenyl-5-methylpyrazole-4-carboxylate (Claisen, *Abstr.*, 1897, i, 440) is

obtained; the *anilide* of the corresponding acid, m. p. 182°, and the *p-toluidide*, m. p. 177°, *α-naphthylamide*, m. p. 168°, and *β-naphthylamide*, m. p. 170°, are described. E. G.

**Acylation of Amines and Phenols.** ADOLF KAUFMANN (*Ber.*, 1909, 42, 3480—3483).—Acylated amines or phenols are obtained rapidly and usually almost quantitatively by adding an acid anhydride to the amine or phenol dissolved in a dry, indifferent solvent, such as ether, light petroleum, benzene, toluene, xylene, or nitrobenzene.

[With RICHARD HÜSSY and A. LUTERBACHER.]—In this way acetanilide, aceto-*o*-toluidide, aceto-*p*-toluidide, *p*-nitroacetanilide, *m*-nitroacetanilide, aceto-*α*-naphthalide, aceto-*β*-naphthalide, acetylanthranilic acid, methylacetanilide, *as*-acetylphenylhydrazine, phenylacetanilide, *p*-acetoxybenzoic acid, *o*-acetoxybenzoic acid, *p*-nitrophenyl acetate, and quinol diacetate have been obtained. In the case of the benzoyl derivatives, the benzoic acid, which is also produced, must be removed by sodium carbonate. Benzanilide and benzoyl-*p*-nitroaniline have been prepared. C. S.

**Nitritoplatato-acids.** KARL A. HOFMANN and KARL BUCHNER (*Ber.*, 1909, 42, 3392—3394).—When *p*-toluidine acts on nitritoplatato-acid, nitrous acid is abstracted from the latter (compare Abstr., 1908, i, 875), with formation of diazoaminotoluene and *toluidine trinitrito-p-toluidinoplatatoate*,  $(N_2O_6Pt, C_7H_9N)H, C_7H_9N$ , which separates in faintly yellow, spear-shaped crystals, decomposes with sparking when heated, and is only slowly attacked by boiling 10% potassium hydroxide solution. When treated with concentrated ammonia solution and alcohol, it yields *p*-toluidine, nitrous acid, and *diamminoplatonitrite*,  $[N_2O_4(NH_3)_2Pt]$ ,

which crystallises in colourless, nacreous leaflets, and, when treated with concentrated hydrochloric acid, yields a *toluidinoplatochloride* to be described later. T. H. P.

**Relations between the Chemical and Physical Characters and the Constitution of Isomeric Amino-derivatives of Camphoric Acid.** GINO ABATI and F. DE NOTARIS (*Gazzetta*, 1909, 39, ii, 219—233).—The authors have prepared the four isomeric *p*-tolylcamphoric acids and the corresponding three imides, the physical properties of which have been examined. The specific refractions,  $R$ , are calculated according to Gladstone's formula.

*α-cis-p-Tolylcamphoric acid*,  $\begin{array}{c} \text{Me} \\ \diagup \\ \text{CO}_2\text{H} \end{array} \text{C}_7\text{H}_{10} \begin{array}{c} \diagdown \\ \text{H} \end{array} \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , prepared by the interaction of camphoric anhydride (1 mol.) and *p*-toluidine (1 mol.) in toluene solution, forms colourless crystals, m. p. 201—209°,  $D_4^{20}$  1.1704,  $[\alpha]_D^{15} + 49.5^\circ$ ,  $R_a$  (in ethyl acetate) 0.4791,  $R_y$  0.5036,  $R_z - R_a$  0.0245.

*α-trans-p-Tolylcamphoric acid*,  $\begin{array}{c} \text{Me} \\ \diagup \\ \text{CO}_2\text{H} \end{array} \text{C}_7\text{H}_{10} \begin{array}{c} \diagdown \\ \text{H} \end{array} \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , prepared by a method similar to that used by Auwers (Abstr., 1900, i, 84) for obtaining *α-trans*-phenylcamphoric acid, forms an amorphous powder, m. p. 183°,  $D_4^{20}$  1.1872,  $[\alpha]_D^{15} - 3.55^\circ$ .

$\beta$ -cis-*p*-Tolylcamphoramic acid,  $\text{CO}_2\text{H} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{C}_7\text{H}_{10} \end{array} \begin{array}{c} \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me} \end{array}$ , prepared by the action of alcoholic potassium hydroxide on *s*-*p*-tolylcamphorimide (*vide infra*), forms white crystals, m. p. 190—196°,  $D_4^{20}$  1.2637,  $[\alpha]_D^{15}$  -64°.

$\beta$ -trans-*p*-Tolylcamphoramic acid,  $\text{CO}_2\text{H} \begin{array}{c} \text{H} \\ \diagup \quad \diagdown \\ \text{C}_7\text{H}_{10} \end{array} \begin{array}{c} \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me} \\ \diagdown \quad \diagup \\ \text{CH}_3 \end{array}$ , prepared similarly to the  $\alpha$ -trans-acid, forms micro-crystals, m. p. 189°,  $[\alpha]_D^{15}$  -13.7°.

*s*-*p*-Tolylcamphorimide,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{CO} \end{array} \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$ , prepared by the interaction of camphoryl chloride and *p*-toluidine in ethereal solution, forms colourless crystals, m. p. 189—190°,  $D_4^{20}$  1.2925,  $[\alpha]_D^{15}$  -24.5°,  $R_a$  (in benzene) 0.4574—0.4598,  $R_\gamma$  0.4754—0.4783,  $R_\gamma - R_a$  0.0180—0.0185.

$\alpha$ -*p*-Tolylcamphorisoimide,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{N}(\text{C}_6\text{H}_4\text{Me}) \\ \diagdown \quad \diagup \\ \text{CO} \end{array} \text{O}$ , prepared by the action of phosphoryl chloride or acetyl chloride on the  $\alpha$ -cis-acid, forms crystals, m. p. 131°,  $D_4^{20}$  1.2103—1.2128,  $[\alpha]_D^{20}$  +16.7°,  $R_a$  (in benzene) 0.4869,  $R_\gamma$  0.5077,  $R_\gamma - R_a$  0.0208.

$\beta$ -*p*-Tolylcamphorisoimide,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{C} \cdot \text{N}(\text{C}_6\text{H}_4\text{Me}) \end{array} \text{O}$ , prepared from the  $\beta$ -cis-acid, has m.p. 146°,  $D_4^{20}$  1.209,  $[\alpha]_D^{15}$  +7.1°.

The *p*-tolylcamphoric acids are analogous in both their chemical and their physical properties to the corresponding phenylcamphoramic acids. For example, the m. p.'s of the two series of acids are as follows :

	Phenylcamphoramic.	<i>p</i> -Tolylcamphoramic.
$\alpha$ -cis-Acid.....	203—204°	201—209°
$\alpha$ -trans-Acid .....	183—183.5	183
$\beta$ -cis-Acid... ..	196	190—196

T. H. P.

**Electrolytic Reduction of the Condensation Products of Aldehydes and Amines.** KURT BRAND (*Ber.*, 1909, 42, 3460—3462).—Benzylaniline is obtained in good yield by the electrolytic reduction of benzylideneaniline. The anode is a lead plate which is inclosed in a porous pot in a beaker; the cathode is a lead cylinder. The liquid at the anode is a saturated solution of sodium carbonate, and at the cathode a solution of 18 grams of benzylideneaniline and 15 grams of sodium acetate in 200 c.c. of alcohol and 30 c.c. of water. The reduction is effected at 80° at 6—8 volts and a current density of 0.015 to 0.02 ampere per sq. cm.

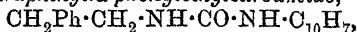
*p*-Methoxybenzylideneaniline is reduced in a similar way to *p*-methoxybenzylaniline.

C. S.

**Amines. I. Synthesis of Phenylethylmethylamine.** TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1909, 42, 340—353).—This investigation has been undertaken on account of the importance of phenylethylamine and *p*-hydroxyphenylethylamine in

physiological chemistry. In the present paper a description is given of phenylethylmethylamine and its derivatives.

When phenylethylamine is treated with methyl iodide there are produced the *hydriodide*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HI}$ , which becomes brown above  $190^\circ$  and decomposes at  $235\text{--}236^\circ$ , and *phenylethyltrimethylammonium iodide*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ , m. p.  $227^\circ$ , which forms colourless plates.  $\beta$ :1-Naphthyl- $\alpha$ -phenylethylcarbamide,

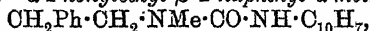


m. p.  $209\text{--}210^\circ$ , prepared by the action of  $\alpha$ -naphthylcarbimide on phenylethylamine, crystallises in needles. *Benzenesulphonylphenylethylamine*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$ , m. p.  $68\text{--}69^\circ$ , forms tabular crystals. *p-Toluenesulphonylphenylethylamine*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p.  $65\text{--}66^\circ$ , crystallises in radiating needles. *Benzenesulphonylphenylethylmethylamine*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{SO}_2\text{Ph}$ , is obtained as a heavy oil by the action of methyl iodide on the sodium derivative of benzenesulphonylphenylethylamine; when heated with concentrated hydrochloric acid at  $150\text{--}160^\circ$ , it yields *phenylethylmethylamine*,



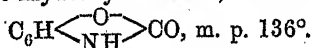
b. p.  $112\cdot5\text{--}115^\circ/36\text{--}40$  mm., a strong base which absorbs carbon dioxide from the air and yields precipitates with phosphotungstic acid and bismuth potassium iodide. The double compound of this amine with mercuric chloride melts at  $172\text{--}173^\circ$ . The *hydrochloride*, m. p.  $152\text{--}154^\circ$ , crystallises in plates containing  $2\text{H}_2\text{O}$ . The *picrate*, m. p.  $141^\circ$ , forms prismatic crystals. The *picrolonate*, m. p.  $217\text{--}218^\circ$ , forms slender prisms or large, tabular crystals. The *platinichloride* and the *hydrogen oxalate* melt at  $212^\circ$  (decomp.) and  $183\text{--}184^\circ$  (decomp.) respectively.

$\alpha$ -Phenylethyl- $\alpha$ -methylcarbamide,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $141^\circ$ , obtained by the action of potassium cyanate on phenylethylmethylamine, forms colourless plates.  $\beta$ -Phenyl- $\alpha$ -phenylethyl- $\alpha$ -methylcarbamide,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CO}\cdot\text{NHPh}$ , m. p.  $104\text{--}105^\circ$ , prepared by treating phenylethylmethylamine with phenylcarbimide, crystallises in rectangular plates.  $\alpha$ -Phenylethyl- $\beta$ -2-naphthyl- $\alpha$ -methylcarbamide,



m. p.  $105\text{--}106^\circ$ , forms rosettes of microscopic needles.  $\beta$ -Phenyl- $\alpha$ -phenylethyl- $\alpha$ -methylthiocarbamide,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CS}\cdot\text{NHPh}$ , m. p.  $113\text{--}114^\circ$ , crystallises in long prisms. E. G.

**Conversion of Aromatic Acid Azoimides into Arylcarbimides.** RICHARD STORMER (*Ber.*, 1909, 42, 3133—3134. Compare Schroeter, this vol., i, 617).—The conversion of aromatic acid azoimides into arylcarbimides has been observed some ten years ago, and the results have been published in Dissertations 1901—1908. Heating the azoimide with dry benzene or toluene is a convenient method for the preparation of certain carbimides on the small scale. The following compounds have been prepared: *m*-phenylenedicarbimide, m. p.  $51^\circ$ ; *o*-methoxyphenylcarbimide, an oil; *m*-nitrophenylcarbimide, m. p.  $49^\circ$ . *o*-Hydroxybenzazide, under similar treatment, yields the urethane,



J. J. S.

**New Method of Formation of Phenolic Ethers of Glycerol.** FRITZ EHLOTZKY (*Monatsh.*, 1909, 30, 663—671. Compare Shirkovitch, *Abstr.*, 1908, i, 978; Hantzsch and Vock, *Abstr.*, 1903, i, 664).—The author has prepared the *p*-chlorophenyl, *o*-chlorophenyl, and 5-chloro-*m*-tolyl ethers of glycerol by the interaction of the phenols and glycerol in presence of fused sodium acetate. The yield obtained with *p*-chlorophenol is considerably greater than those given by the other two compounds, whilst with *s*-trichlorophenol no glycerol ether is formed. These results are in agreement with those of V. Meyer and his pupils, who found that the presence of an ortho-substituent usually delays or completely prevents reaction.

*p*-Chlorophenyl glycerol ether,  $C_6H_4Cl \cdot O \cdot C_3H_5(OH)_2$ , forms white crystals, m. p.  $76^\circ$ , dissolves in concentrated sulphuric acid with a faint red coloration, which with potassium nitrite solution changes to reddish-violet, and then becomes yellow on supersaturation with potassium hydroxide solution and dilution. The *dibenzoyl* derivative,  $C_6H_4Cl \cdot O \cdot C_3H_5(OBz)_2$ , separates in a felted mass of white needles, m. p.  $83.5^\circ$ .

*p*-Chlorophenol forms a *benzoyl*-derivative crystallising in silky leaflets, m. p.  $88^\circ$ .

*o*-Chlorophenyl glycerol ether,  $C_6H_4Cl \cdot O \cdot C_3H_5(OH)_2$ , forms white crystals, m. p.  $56^\circ$ , and with concentrated sulphuric acid and potassium nitrite gives a yellow coloration which persists on addition of potassium hydroxide solution to the liquid and dilution. Its *dibenzoyl* derivative,  $C_{22}H_{19}O_5Cl$ , forms short bundles of white crystals, m. p.  $59-60^\circ$ .

5-Chloro-*m*-tolyl glycerol ether,  $C_6H_2MeCl \cdot O \cdot C_3H_5(OH)_2$ , separates in white, granular crystals, m. p.  $83^\circ$ , and with concentrated sulphuric acid and potassium nitrite gives a dirty green coloration, which is changed to yellow by addition of potassium hydroxide solution and dilution.

None of these three ethers gives a coloration with ferric chloride.

T. H. P.

**Derivatives of 1:2-Dimethylbenzene [*o*-Xylene].** EMIL DIEPOLDER (*Ber.*, 1909, 42, 2916—2923).—5-Nitro-*o*-4-xyleneol is obtained by nitrating *o*-4-xyleneol, dissolved in acetic acid, together with the 3:5-nitro-derivative and a small quantity of tarry matter. It crystallises in thin, yellow rhombs, m. p.  $87^\circ$ , and has an odour similar to *o*-nitrophenol; the potassium salt forms bright red prisms in stellar aggregates, whilst the sodium salt forms flat, red needles. When heated with ammonia with the addition of ammonium chloride for some time at  $140-150^\circ$ , the nitro-compound is converted into 5-nitro-*o*-4-xylidine, which crystallises in microscopic, six-sided prisms, m. p.  $140^\circ$ . The structure of this compound is proved by the fact that on replacing the amino-group by hydrogen the 4-nitro-*o*-xylene, m. p.  $29^\circ$ , described by Jacobsen (*Ber.*, 1884, 17, 160) is obtained.

When *o*-4-xyleneol is coupled with benzenediazonium sulphate, a mixture of 83% symmetric and 17% vicinal quinonephenylhydrazones is formed, which is separated by crystallisation from alcohol. The phenylhydrazone of *c*-4:5-xyloquinone, recently described by Auwers

and Heyden (this vol., i, 438) as crystallising in dark orange, glistening needles, more commonly separates in red needles with a violet reflex. The 3-phenylhydrazone of o-3 : 4-xyloquinone crystallises in large, brown plates or prisms.

5-Amino-o-4-xylenol, obtained by reducing the corresponding nitro-compound, crystallises from ether in glistening plates, and forms colourless rhombs when sublimed. It turns brown above 165°, m. p. 173—175°. The hydrochloride forms silky, glistening needles, m. p. 250°. When oxidised with potassium dichromate in sulphuric acid solution, 1 : 2-dimethyl-4 : 5-benzoquinone is formed. This crystallises in long, red needles, which are greenish-yellow in transmitted light, m. p. 102°. It can also be obtained in yellow plates, which slowly become red and give the red needles when recrystallised. This

corresponds with the isomeric modification : 
$$\begin{array}{c} \text{CMe}:\text{CH}\cdot\text{C}\cdot\text{O} \\ \text{CMe}:\text{CH}\cdot\text{C}\cdot\text{O} \end{array}$$

2 : 3-Dimethylphenazine, prepared by the interaction of the quinone with o-phenylenediamine, separates in small, yellow crystals, m. p. 173°, which dissolve in concentrated sulphuric acid with a red coloration. E. F. A.

Action of Sulphites on Aromatic Amino- and Hydroxyl Compounds. VII. Application of the Sulphite Reaction to Some ana-(1 : 5)-Derivatives of Naphthalene. HANS TH. BUCHERER and A. UHLMANN (*J. pr. Chem.*, 1909, [ii], 80, 201—241. Compare Abstr., 1904, i, 309).—The hitherto unknown 5-amino- $\alpha$ -naphthol-4-sulphonic acid has been prepared, since apparently it fulfils the requirements of an aminonaphtholsulphonic acid suitable for the production of polyazo-dyes like diamine-black, namely, coupling of the acid (2 mols.) with a diazotised *p*-diamine must yield a diazo-derivative in which the sulpho- and the azo-groups are in different rings of the naphthalene nucleus, in order that the existent amino-groups may be capable of diazotisation.

The preparation of the acid was first attempted by sulphonating 1 : 5-naphthylenediamine, but the sulpho-group enters position 2 and not 8, the proof being based on the fact that, after the naphthylenediaminesulphonic acid has been converted into an aminonaphthol-sulphonic acid by the hydrogen sulphite reaction, the sulpho-group is not eliminated by 20% hydrochloric acid, showing that it is not para to the hydroxyl group.

A successful result is obtained by using Nietzki and Zübelen's method (Abstr., 1889, 513), in which naphthionic acid, by the successive operations of acetylation of its sodium salt by acetic anhydride, nitration in concentrated sulphuric acid, and reduction, is converted into 1 : 5-naphthylenediamine-8-sulphonic acid. This acid is changed by the hydrogen sulphite process into 5-amino- $\alpha$ -naphthol-4-sulphonic acid, the orientation of which is proved by its conversion into 5-amino- $\alpha$ -naphthol by 20% hydrochloric acid. The 5-nitro-1-acetylamino-naphthalene-4-sulphonic acid obtained in the preceding operations is reduced by zinc dust and hydrochloric acid below 30° to 5-acetyl-amino- $\alpha$ -naphthylamine-8-sulphonic acid, which is converted by the

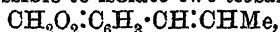
hydrogen sulphite process into 5-amino-*a*-naphthol-8-sulphonic acid. The latter is further changed by the hydrogen sulphite into 1:5-dihydroxynaphthalene-8-sulphonic acid, which is converted by ammonium sulphite and excess of ammonium hydroxide into 1:5-naphthylene-diamine-8-sulphonic acid.

1:5-Dihydroxynaphthalene, sulphonated by concentrated sulphuric acid at 50—60°, yields a mixture of 1:5-dihydroxynaphthalene-2-sulphonic acid and the corresponding 4-sulphonic acid.

5-Amino-*a*-naphthol-4-sulphonic acid couples with tetrazotised benzidine to form a dark blue dye; when this is diazotised on the fibre and developed with  $\beta$ -naphthol, the dye bleeds freely, and only a pale brown shade is produced. The acid therefore does not fulfil expectations. C. S.

**Stereochemistry of Ethylene Derivatives: Two Stereoisomeric *iso*Safroles.** PAUL HOERING and FRITZ BAUM (*Ber.*, 1909, 42, 3076—3088).—The allyl side-chain in various unsaturated phenolic ethers is readily transformed into a propylene side-chain by the action of alcoholic potassium hydroxide (compare Eykman, *Abstr.*, 1890, 137, 749). The propylene derivatives thus obtained should exist in two stereoisomeric forms, but so far no such cases of isomerism have been established. In several cases of supposed stereoisomerism, for example, anethole and esdragole, the compounds have been shown to be structural isomerides.

It has been found possible to isolate two *isosafroles*,



from commercial *isosafrole*, which also contains unaltered safrole.

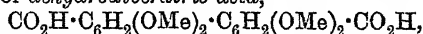
$\beta$ -*iso*Safrole, which is the chief constituent, has b. p. 123°/11.5 mm.,  $D_{17.5}^{21}$  1.1227, and  $n_D^{18}$  1.5786, and is most readily isolated in the form of its picrate (m. p. 74°: compare Bruni and Tornani, *Abstr.*, 1904, i, 875), which is decomposed when boiled with solvents in which picric acid is sparingly soluble, or when ammonia is led into its alcoholic solution.

$\alpha$ -*iso*Safrole has b. p. 116.2—116.3°/13.5 mm., or 242.2—242.5°/760 mm.,  $D_{18.5}^{18}$  1.1073, and  $n_D^{18}$  1.5678. It is best isolated from the first fractions obtained by repeated fractionation from a Stephan flask. Safrole can be removed by shaking an ethereal solution of the *isosafrole* with a 10% aqueous solution of mercuric acetate (Balbiano, this vol., i, 401). Small quantities of  $\beta$ -*isosafrole* can be removed by the addition of picric acid, and then distilling in steam under reduced pressure at 50—55°, when the  $\alpha$ -*isosafrole* distils over, whereas the  $\beta$ -compound remains behind in combination with the picric acid.

The two *isosafroles* resemble one another in chemical properties. They yield the same dibromide and also the same glycol when oxidised. J. J. S.

**Oxidation of Dimethyldehydrodiisoeugenol and of Dimethyldehydrodivanillin.** HENRI HÉRISSEY and G. DOBY (*J. Pharm. Chim.*, 1909, [vi], 30, 289—297).—An attempt to establish an analogy between dehydrodiisoeugenol and dehydrodivanillin, two compounds resulting from the oxidation of isoeugenol and vanillin

respectively (Abstr., 1908, i, 783). The phenols were converted into their methyl ethers by the process already described. Oxidation of dehydrodivanillin dimethyl ether by potassium permanganate leads to the production of *dehydrodiveratric acid*,



in 93–95% yield. This compound forms needles, m. p. about 308° (decomp.), subliming below this temperature. It is very sparingly soluble in the usual solvents. The *dimethyl* ester,  $\text{C}_{20}\text{H}_{22}\text{O}_8$ , crystallises from alcohol in long, silky needles, m. p. 130°.

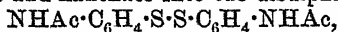
An unexpected result followed when dehydrodiveratriol dimethyl ether was oxidised in the same way, a small yield of veratric acid being obtained. The conclusion is drawn that either the ether does not have the constitution previously ascribed to it, or that the propenyl group exercises an abnormal influence on the course of the oxidation.

W. O. W.

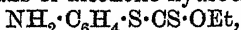
**Preparation of Guaiacol-5-sulphonic Acid and its Salts.** F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 212389).—This acid is prepared free from the para-isomeride by sulphonating acyl derivatives of guaiacol, hydrolysing the product, and removing excess of sulphuric acid. The sulphonic acid of guaiacol carbonate has m. p. 115–117°. *Potassium benzoylguaiacol-5-sulphonate* forms colourless needles readily soluble in water, but the free acid, being deliquescent, was not readily obtained.

F. M. G. M.

***p*-Aminothiophenol [*p*-Aminophenyl Mercaptan].** THEODOR ZINCKE and P. JÖRG (*Ber.*, 1909, 42, 3362–3374).—In the preparation of *p*-acetylaminophenyl mercaptan (compare Leuckart, Abstr., 1890, 603; Hinsberg, Abstr., 1906, i, 654), it is better not to convert the product,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$ , of the interaction of diazotised acetyl-*p*-phenylenediamine and xanthate into the disulphide,

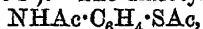


but to convert it by means of alcoholic hydrochloric acid into



which is readily hydrolysed by alcoholic potassium hydroxide and transformed into *p*-aminophenyl mercaptan. Reduction of acetyl-aniline-*p*-sulphonyl chloride by means of zinc dust and hydrochloric acid is a still more simple method of obtaining *p*-acetylaminophenyl mercaptan, which is readily hydrolysed to *p*-aminophenyl mercaptan or its hydrochloride.

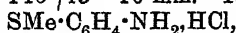
*p*-Aminophenyl mercaptan solidifies as a white, granular, crystalline mass having a faint smell, m. p. 46°, b. p. 140–145°/15–16 mm.; its hydrochloride forms slender needles; the acetyl derivative has m. p. 150° (Hinsberg, *loc. cit.*, gave 154°). The diacetyl compound,



exists in two forms, the one, m. p. 144°, described by Hinsberg, on heating at 155–160° being converted into a *second*, m. p. 132°, which retains its m. p. after repeated fusion and cooling, but when seeded with the first modification is reconverted into this.

*p*-Aminophenyl methyl thioether,  $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , prepared by treating *p*-acetylaminophenyl mercaptan with methyl sulphate and hydrolysing

the *p*-acetylaminophenyl methyl thioether (compare Hinsberg, *loc. cit.*) thus formed by means of alcoholic hydrochloric acid, is an oily liquid with a faint odour, b. p.  $140^{\circ}/15-16$  mm. Its *hydrochloride*,



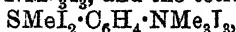
and *sulphate*,  $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \frac{1}{2} \text{H}_2\text{SO}_4$ , were prepared. *p*-Aminophenyl methyl thioether is very reactive; with quinones it behaves like aniline, and yields intensely-coloured compounds; it can be diazotised, and the diazo-salt couples with  $\beta$ -naphthol and is readily converted into the iodide; the hydrochloride is oxidised by ferric chloride, giving a bluish-violet coloration and then a separation of brownish-violet needles with metallic lustre, which are under investigation.

*p*-Acetylaminophenyl methyl sulphoxide,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SOMe}$ , prepared by the action of water on the dibromide (*vide infra*) or by oxidising *p*-acetylaminophenyl methyl thioether by means of hydrogen peroxide, crystallises in white needles or plates, m. p.  $126^{\circ}$ , is converted into *p*-bromoacetanilide by excess of bromine water and with hydrogen bromide yields the *hydrobromide* of *p*-acetylaminophenyl methyl thioether dibromide,  $(\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SBr}_2\text{Me})_2 \cdot \text{HBr}$ , which forms an orange-yellow, crystalline powder, m. p. about  $100^{\circ}$  (decomp.). The *dibromide* itself,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SBr}_2\text{Me}$ , obtained by the action of bromine on *p*-acetylaminophenyl methyl thioether in chloroform solution, forms an orange-yellow, crystalline powder, m. p.  $104^{\circ}$  (decomp.), and when treated with potassium hydroxide liberates iodine with formation of *p*-acetylaminophenyl methyl thioether.

*m*-Bromo-*p*-acetylaminophenyl methyl thioether,  $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{SMe}$ , prepared by the action of concentrated hydrobromic acid on *p*-acetylaminophenyl methyl sulphoxide, crystallises from benzene in colourless leaflets, m. p.  $127^{\circ}$ .

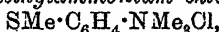
*m*-Chloro-*p*-aminophenyl methyl thioether,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SMe}$ , obtained together with a blue sulphiminoquinone,  $\text{NH} \langle \text{C}_6\text{H}_2 \rangle \text{SMeCl} (?)$ , by the action of concentrated hydrochloric acid on *p*-acetylaminophenyl methyl sulphoxide, is a colourless oil with a faint odour; the *hydrochloride*,  $\text{C}_7\text{H}_9\text{NSCl}_2$ , and the *acetyl* derivative,  $\text{C}_9\text{H}_{10}\text{ONSCl}$ , m. p.  $128^{\circ}$ , were prepared.

*p*-Methylthiolphenyltrimethylammonium iodide,  $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_3\text{I}$ , prepared by heating either *p*-aminophenyl methyl thioether with methyl iodide or *p*-acetylaminophenyl methyl thioether with methyl iodide and methyl alcohol, crystallises in colourless, rhombic plates, m. p.  $180-184^{\circ}$  (decomp.), and by addition of iodine is converted into the di-iodide,  $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_3\text{I}_2$ , and the tetraiodide,



neither of which gave concordant numbers on analysis.

*p*-Methylthiolphenyltrimethylammonium chloride,



prepared from the preceding compound and freshly precipitated silver chloride, forms colourless, unstable needles, m. p.  $193-194^{\circ}$ . The *platinichloride* was analysed.

*p*-Dimethylaminophenyl methyl thioether,  $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , prepared either by heating *p*-methylthiolphenyltrimethylammonium chloride at  $200^{\circ}$  or by the action of methyl alcoholic hydrogen chloride on

*p*-aminophenyl methyl thioether, forms white leaflets, m. p. 23°; its *hydrochloride* was analysed.

Oxidation of *p*-acetylaminophenyl mercaptan by means of ferric chloride in alcoholic solution yields the  $\alpha$ -form of diacetyldiaminodiphenyl disulphide,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , m. p. 179–180° (Hinsberg, *loc. cit.*, gave 182°), which has been kept for ten months without alteration.

T. H. P.

**Trithiophloroglucinol.** JACQUES POLLAK and J. CARNIOL (*Ber.*, 1909, 42, 3252–3253).—*Trithiophloroglucinol*,  $\text{C}_6\text{H}_6\text{S}_3$ , prepared by reducing benzene-1:3:5-trisulphonyl chloride with tin and hydrochloric acid, is a white powder, m. p. 56–58°, having a characteristic odour; it readily undergoes oxidation, and gives an orange-red precipitate with lead acetate. The *triacetate*,  $\text{C}_{12}\text{H}_{12}\text{O}_3\text{S}_3$ , crystallises in white needles, m. p. 73–74°. The *trimethyl ether*,  $\text{C}_9\text{H}_{12}\text{S}_3$ , forms slender needles, m. p. 66–68°.

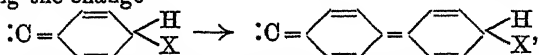
W. H. G.

**Xylene Thiocyanates.** Mlle. MARIE STRZELECKA (*Bull. Acad. sci. Cracow*, 1909, 731–734).—The following substances, obtained from xylol or xylene bromides and potassium thiocyanate in dilute alcohol, have an unpleasant, piercing odour. *p*-Xylol thiocyanate,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{SCN}$ , has m. p. 21.5–22.5. *p*-Xylylene thiocyanate,  $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{SCN})_2$ , m. p. 134°, has been erroneously described as *p*-xylol thiocyanate (*Abstr.*, 1902, i, 470). *m*-Xylol thiocyanate, b. p. 170°/30 mm., is a yellow, oily liquid. *m*-Xylylene thiocyanate, m. p. 60°, crystallises in colourless needles. *o*-Xylol thiocyanate has m. p. 18–18.5°, and *o*-xylylene thiocyanate has m. p. 79°.

C. S.

**Analogues of Triphenylmethyl in the Diphenyl Series.** WILHELM SCHLENK [with TOBIAS WEICKEL] (*Annalen*, 1909, 368, 295–304).—The effect of gradually replacing the phenyl groups of triphenylcarbinol by diphenyl has been investigated with the object of obtaining information on the cause of the colour of triphenylcarbinol salts.

It is found that the replacement of each phenyl group by the diphenyl residue is accompanied by an increase in the depth of colour; thus, solutions of triphenylcarbinol, 4-phenyltriphenylcarbinol, 4:4'-diphenyltriphenylcarbinol, and 4:4':4''-triphenyltriphenylcarbinol in a mixture of acetic and sulphuric acids are yellow, yellowish-red, red, and bluish-red respectively. The conclusion is drawn, therefore, that the colour of the salts of triphenylcarbinol is not due to a quinonoid structure, since a sudden and marked change of colour representing the change



which must necessarily occur at one stage in the passage of triphenylcarbinol to 4:4':4''-triphenyltriphenylcarbinol, is not observed.

4-Phenyltriphenylcarbinol,  $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CPh}_2\cdot\text{OH}$ , prepared by Grignard's method from (1) benzophenone and *p*-iododiphenyl; (2) bromobenzene and methyl diphenyl-*p*-carboxylate, crystallises in needles and plates, m. p. 136°; when acted on by acetyl chloride it yields

4-phenyltriphenylmethyl chloride,  $C_6H_4Ph \cdot CPh_2 \cdot Cl$ , which crystallises in cubes, m. p.  $147.5^\circ$ .

4:4'-Diphenyltriphenylcarbinol,  $CPh(C_6H_4Ph)_2 \cdot OH$ , prepared from diphenylbenzophenone and bromobenzene, crystallises in needles, m. p.  $151^\circ$ ; the corresponding chloride,  $C_{31}H_{23}Cl$ , has m. p.  $131.5^\circ$ .

4:4':4''-Triphenyltriphenylcarbinol,  $C(C_6H_4Ph)_3 \cdot OH$ , may be prepared by Grignard's method from (1) methyl diphenyl-*p*-carboxylate and *p*-iododiphenyl; (2) 4:4'-diphenylbenzophenone and *p*-iododiphenyl, and by the method of Friedl and Crafts from diphenyl and carbon tetrachloride; it crystallises in white needles, m. p.  $207-208^\circ$ . 4:4':4''-Triphenyltriphenylmethyl chloride,  $C_{37}H_{27}Cl$ , forms white needles, m. p.  $195^\circ$ .

*p*-Iododiphenyl,  $C_{12}H_9I$ , prepared by treating diphenyl-4-diazonium chloride with potassium iodide, has m. p.  $112^\circ$ , b. p.  $222^\circ/40$  mm.,  $198^\circ/11$  mm.

Methyl diphenylcarboxylate,  $C_{14}H_{12}O_2$ , has m. p.  $117.5^\circ$ .

W. H. G.

Preparation of *o*-Dihydroxyphenylethanolamine. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 212206. Compare Barger and Jowett, Trans., 1905, 87, 971).— $\beta$ -Bromo- $\alpha$ -3:4-trihydroxy- $\alpha$ -phenylethane,  $C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2Br$ , an unstable, viscous oil, is obtained by treating  $\alpha\beta$ -dibromo-3:4-methylenedioxy- $\alpha$ -phenylethane with phosphorus pentachloride (2 mols.) and heating at  $105^\circ$  during ten to twenty hours.  $\alpha$ -3:4-Trihydroxy- $\alpha$ -phenylethylmethylamine,  $C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NHMe$ , is obtained when the foregoing compound is treated with seven times its weight of a cold 40% aqueous methylamine solution. The methylamine in this reaction may be replaced by other alkylamines or by ammonium hydroxide.

F. M. G. M.

Preparation of Acid Anhydrides. ADOLF KAUFMANN and A. LUTERBACHER (Ber., 1909, 42, 3483-3485).—A solution of equal molecular quantities of benzoic acid and acetic anhydride in dry benzene is boiled for six hours and fractionally distilled. The last fraction, b. p.  $347-348^\circ$ , is pure benzoic anhydride in 81.4% yield. By using xylene and  $2\frac{1}{2}$  mols. of acetic anhydride, the yield is increased to 86% (compare Autenrieth, Abstr., 1901, i, 185).

C. S.

Preparation of Substituted Aromatic Carboxylic Acids from the Corresponding Aldehydes. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 211959).—The oxidation of aromatic aldehydes to the corresponding acids proceeds very smoothly when sodium hypochlorite and excess of alkali are the reagents employed.

*m*-Nitrobenzaldehyde (151 parts) is slowly added to a solution of sodium hydroxide (40 parts) and sodium hypochlorite (71 parts available chlorine). Care must be taken at first that the reaction does not become violent, but finally the solution is warmed until the hypochlorite is decomposed; on cooling, the greater part of the sodium *m*-nitrobenzoate crystallises out in a pure condition.

F. M. G. M.

**Synthesis of the Two Optically Active Prolines.** EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1909, 42, 2989—2997).—Proline was hitherto only known in the form of the racemic compound, and the *l*-compound obtained by protein hydrolysis. *m*-Nitrobenzoylproline has been synthesised from  $\delta$ -*m*-nitrobenzoylaminovaleric acid, and resolved into its optically active components by means of cinchonine. These when boiled with hydrochloric acid are decomposed into *m*-nitrobenzoic acid and the optically active prolines, which are similar in properties to the natural *l*-proline. The action of ammonia and of methylamine on  $\alpha$ -bromo- $\delta$ -*m*-nitrobenzoylaminovaleric acid has been studied, *m*-nitrobenzoylornithine and its methyl derivative being formed respectively.

*$\alpha$ -Bromo- $\delta$ -m-nitrobenzoylaminovaleric acid,*

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot [\text{CH}_2]_2 \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$ , obtained by acting on  $\delta$ -*m*-nitrobenzoylaminovaleric acid with bromine and red phosphorus, crystallises in bunches of colourless needles, which sinter about 120°, m. p. 125°. The bromine is eliminated on treatment in the cold with saturated aqueous ammonia, and  $\delta$ -*m*-nitrobenzoylornithine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot [\text{CH}_2]_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , obtained in the form of a colourless, crystalline powder, m. p. 250° (decomp.). Aqueous methylamine acts on the bromo-compound to form  $\delta$ -*m*-nitrobenzoylamino- $\alpha$ -methylaminovaleric acid,

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot [\text{CH}_2]_2 \cdot \text{CH}(\text{NHMe}) \cdot \text{CO}_2\text{H}$ , which likewise crystallises in colourless needles; these turn brown at 200°, m. p. 240° (decomp.).

When the bromo-compound is kept at 37° with sodium hydroxide, *dl*-*m*-nitrobenzoylproline,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{N} \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CH}(\text{CO}_2\text{H}) \end{smallmatrix} \text{CH}_2$ , is formed. This crystallises in microscopic, rhombic plates, m. p. 90—92°. The cinchonine salt is a colourless, crystalline substance, m. p. 150°, to a brown substance, that of the *d*-isomeride being the first to separate from aqueous solution. When hydrolysed with sodium hydroxide, *d*-*m*-nitrobenzoylproline is obtained. It crystallises in microscopic prisms in stellar aggregates, has m. p. 137—140°, and  $[\alpha]_D^{20} + 12.0^\circ (\pm 0.5^\circ)$ . *d*-Proline is obtained, on heating the above with 10% hydrochloric acid for six hours, mixed with some racemic compound, from which it is separated by treatment of the mixed copper salts with alcohol. It crystallises in prisms, m. p. 215—220° (decomp.), and has  $[\alpha]_D + 81.5^\circ (\pm 0.5^\circ)$ . The cinchonine mother liquors contain the salt of *l*-nitrobenzoylproline, from which *l*-proline can be obtained in the same manner as described for the *d*-isomeride. It has the same crystalline form, m. p. 215—220°, and  $[\alpha]_D^{20} - 80.4^\circ (\pm 0.5^\circ)$ . This is a little higher than the value recorded ( $-77.4^\circ$ ) for the natural amino-acid.

E. F. A.

**Preparation of *o*-Aminobenzonitrile and its Substitution Products.** KALLE & Co. (D.R.-P. 212207).—Iron filings (500 parts), 50 c.c. of acetic acid (50%), and water (1000 parts) are mixed and kept at a temperature of 65° during half an hour; *o*-nitrobenzonitrile (148 parts) is then slowly added, and the temperature kept below 70°. When reduction (which proceeds rapidly) is complete, the liquid is

rendered alkaline with sodium carbonate, filtered hot, and a 10% solution of sodium chloride stirred in; on cooling, the *o*-aminobenzonitrile separates as colourless leaflets. F. M. G. M.

**Introduction of the Nitroso-group into the Nucleus of *N*-Alkylated Esters of Anthranilic Acid.** JOSEF HOUBEN (*Ber.*, 1909, 42, 3188—3196).—A further study of the method of Houben, Brassert, and Ettinger (compare this vol., i, 645) for preparing derivatives of 5-nitrosoanthranilic acid. The author proposes to carry out further investigations of these compounds, as well as of derivatives of *p*-quinoneoximecarboxylic acid, which in regard to the production of dyes behaves as though it were a 5-nitrososalicylic acid. In certain conditions it is possible to introduce the nitroso-group directly into the nucleus of salicylic acid. Direct nitrosylation in the nucleus is impossible in the case of anthranilic acid derivatives, in which both the hydrogen atoms of the amino-group are replaced by alkyl groups, as in dimethylantranilic acid. The author considers that this must be due to some steric rather than chemical influence. It is not a peculiarity of the carboxyl group, since other dialkylamino-compounds with an *ortho*-substituent are also incapable of nitrosylation.

The 5-nitroso-derivative of methylantranilic acid may be prepared with 84% yield by acting on the nitrosoamine with fuming hydrochloric acid; this is in harmony with the idea that the production of the nitroso-derivative depends on the primary formation of the nitrosoamine.

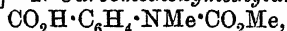
The nitrosylation of phenyl methylantranilate was found to present no difficulty, in spite of the largeness of the group attached to the carboxyl. For the preparation of the phenyl ester it was necessary to devise a special method, since it cannot be obtained from anthranilic acid and phenol.

*Attempt to Nitrosylate Methyl Dimethylantranilate.* [With LEO ETTINGER].—Neither the ester nor its solutions show any trace of fluorescence; in this they differ from the esters of anthranilic and methylantranilic acids. The desired nitroso-derivative could not be obtained by treatment with sodium nitrite either in dilute or in concentrated hydrochloric acid, or in alcoholic hydrogen chloride. On long standing, a nitroso-compound was obtained as a green, flocculent precipitate, but it was not a derivative of dimethylantranilic acid. Similar experiments with the free acid were also unsuccessful.

*Methyl methylethylantranilate* is obtained by heating methyl methylantranilate for three to four days with ethyl bromide in a sealed tube at 95°. The white, crystalline product is extracted with ether and decomposed with sodium carbonate in aqueous solution, whereon the ester is obtained as a yellow oil, b. p. 142—143°/16 mm. It does not fluoresce. It does not yield a nitroso-derivative by any of the above methods.

The transformation of *o*-methylnitrosoaminebenzoic acid into 5-nitrosomethylantranilic acid is effected when the nitrosoamine is dissolved in fuming hydrochloric acid; the dark red solution deposits the hydrochloride of the nitroso-acid as a yellow precipitate.

[With R. FREUND.]—*N*-Carbomethoxymethylanthranilic acid,



is obtainable from the aromatic amino-acid, methylanthranilic acid, by the method which E. Fischer has shown to be applicable to phenolcarb-oxylic acids (Abstr., 1908, i, 892; 1909, i, 161, 309) and to aliphatic amino-acids (Abstr., 1903, i, 799). Methylanthranilic acid is dissolved in the equivalent quantity of potassium carbonate and shaken with methyl chlorocarbonate. The compound forms white crystals, m. p. 137—138°; yield almost theoretical. *N*-Carbomethoxymethylanthranilic acid, obtained in a similar way, forms white needles, m. p. 118°. When either of these urethanes is heated for some hours with acetic anhydride, or heated alone for a short time at 220°, the anhydride of *N*-methyl-isatoic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} - \text{O} \end{smallmatrix}$ , is obtained in large crystals or in yellow needles, m. p. 177°. When heated with concentrated sulphuric acid, *N*-methylanthranilic acid is produced almost quantitatively, and if the temperature is further raised, methylaniline is eventually formed.

[With ERICH KELLNER.]—On heating the above anhydride with phenol, phenyl *N*-methylanthranilate is obtained in yellow needles of m. p. 70—71°; yield over 60%. The substance shows a sky-blue fluorescence in solution; it is less basic than the alkyl esters of the same acid. Phenyl 5-nitrosomethylanthranilate may be obtained by preparing the nitrosoamine of the above phenyl ester and acting on that compound with concentrated hydrochloric acid, but is best prepared (56% yield) by treating the solution of the ester in fuming hydrochloric acid with sodium nitrite. The substance forms lustrous, green needles, and has m. p. 135—136°.

[With WALTER BRASSERT and LEO ETTINGER.]—Methyl 5-nitroso-*N*-ethylanthranilate forms small, green needles of m. p. 91°; yield 48%. Ethyl *N*-ethylanthranilate, prepared by esterifying ethylanthranilic acid with alcohol and sulphuric acid, is an almost colourless oil, which has b. p. 142°/11 mm. or 150—151°/16 mm. Ethyl 5-nitroso-*N*-ethylanthranilate forms a felted mass of long, shining green threads, and has m. p. 87—88°; yield 41%.  
R. V. S.

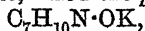
### 6-Nitro-4-sulpho-3-toluic Acid and Some of its Derivatives.

WILLIAM J. KARSLAKE and R. C. HUSTON (*J. Amer. Chem. Soc.*, 1909, 31, 1057—1060).—It has been shown by Karslake and Bond (this vol., i, 231) that when 6-nitro-*m*-xylene-4-sulphonic acid is oxidised with a cold alkaline solution of potassium permanganate, the potassium salts of 4-nitro-2-sulpho-5-toluic, 6-nitro-4-sulpho-3-toluic, and 6-nitro-4-sulphoisophthalic acids are obtained. As 6-nitro-4-sulpho-3-toluic acid has not been described previously, a further study of this acid and its derivatives has been carried out.

6-Nitro-4-sulpho-3-toluic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{SO}_3\text{H}) \cdot \text{CO}_2\text{H} \cdot \text{H}_2\text{O}$ , m. p. 34—37°, forms long, flat, colourless needles, and when heated at 110°, is converted into the anhydrous form, m. p. 150·7° (corr.). The chloride, m. p. 90·2° (corr.), and the diamide, m. p. 273—274°, crystallise in prismatic plates. The dianilide, m. p. 204·8° (corr.),

forms small, yellow plates. The *di-o*-, *-m*-, and *-p-toluidides* melt at  $238.7^{\circ}$  (corr.),  $208.8^{\circ}$  (corr.), and  $241.8^{\circ}$  (corr.) respectively. The *dimethyl* ester forms white crystals, and chars without melting at  $302-305^{\circ}$ . The *potassium*, potassium hydrogen, silver, *sodium*, sodium hydrogen, calcium, calcium hydrogen, barium, barium hydrogen, strontium, strontium hydrogen, ammonium, magnesium, zinc, copper, and lead salts are described. E. G.

**Derivatives of Hydroxyhexahydrobenzoic** [*cycloHexan-1-ol-1-carboxylic*] Acid. P. JOSEPH TARBOURIECH (*Compt. rend.*, 1909, 149, 604-606).—A study of Bucherer's acid obtained from *cyclohexanone* (Abstr., 1894, i, 366). The nitrile is most conveniently prepared by adding *cyclohexanone* to a very concentrated solution of potassium cyanide, when the *potassium* derivative,



separates; treatment of this with 10% hydrogen chloride yields the nitrile as an oil, b. p. about  $110^{\circ}/18$  mm. The *potassium* salt of the acid crystallises in spangles containing  $1H_2O$ .

The *methyl* ester,  $C_6H_{11}O\cdot CO_2Me$ , has b. p.  $103^{\circ}/17$  mm.; the *ethyl* ester has b. p.  $111^{\circ}/18$  mm.; the *isoamyl* ester has b. p.  $142^{\circ}/18$  mm.; the *amide* has m. p.  $124^{\circ}$ . Treatment of the methyl ester with magnesium methyl iodide leads to the formation of *cyclohexanolpropan-β-ol*,  $C_6H_{10}(OH)\cdot CMe_2\cdot OH$ , crystallising in needles, m. p.  $83^{\circ}$ , and having a camphoraceous odour. On oxidation with chromium trioxide, this yields *propanone* and *cyclohexanone*, whilst under certain conditions it loses water, forming a pinacolin with a hydrocarbon.

W. O. W.

**Oxalyl Chloride. II. Action of Oxalyl Chloride on Dimethylaniline.** HERMANN STAUDINGER and H. STOCKMANN (*Ber.*, 1909, 42, 3485-3496. Compare Abstr., 1908, i, 938).—Since oxalyl chloride is nearly analogous to carbonyl chloride, its behaviour towards dimethylaniline has been examined.

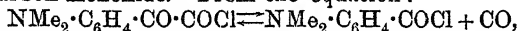
When ethereal solutions of oxalyl chloride (1 mol.) and dimethylaniline (2 mol.) are mixed and kept at  $0^{\circ}$  for fifteen hours, a quantitative formation of *p*-dimethylaminophenylglyoxyl chloride,



and dimethylaniline hydrochloride occurs. The former compound exists only in solution, and its presence is detected by converting it into *p*-dimethylaminophenylglyoxylic acid and the corresponding methyl ester and anilide. At higher temperatures, particularly in benzene solution, *p*-dimethylaminophenylglyoxyl chloride decomposes quantitatively into carbon monoxide and *p*-dimethylaminobenzoyl chloride, a portion of which condenses with dimethylaniline to form crystal-violet.

Ethereal or, better, benzene solutions of oxalyl chloride (1 mol.) and dimethylaniline (4 mols.) react in the cold as above, but when they are kept at  $0^{\circ}$  for fifteen hours and then heated on the water-bath, the initially formed *p*-dimethylaminophenylglyoxyl chloride reacts in two ways: on the one hand, yielding tetramethyl-*p*:*p'*-diaminobenzil, and on

the other, decomposing into carbon monoxide and dimethylaminobenzoyl chloride. This condenses with dimethylaniline to Michler's ketone, which in its turn reacts with dimethylaniline hydrochloride to form crystal-violet under the condensing influence of a part of the dimethylaminobenzoyl chloride, which is thereby converted into dimethylaminobenzoic acid. The products of the whole reaction, therefore, are chiefly crystal-violet and smaller quantities of dimethylaminobenzoic acid and tetramethyl-*p*:*p*'-diaminobenzil. The yield of the last is only 17%, but is increased to 35% by using a large excess of dimethylaniline (10 mols.) to absorb rapidly the liberated hydrogen chloride. A still better way is to work under pressure in an atmosphere of carbon monoxide. From the equation:



it is evident that by increasing the concentration of the carbon monoxide, the dissociation of the dimethylaminophenylglyoxyl chloride must be diminished, and consequently a larger amount of this substance is available for the production of tetramethyldiaminobenzil. It is actually found that the yield of the latter is 50% at 45 atmospheres, and 87% at 150 atmospheres, when oxalyl chloride and dimethylaniline, in the proportion 1:10, are kept at 0° for fifteen hours, and are then heated for six hours on the water-bath in an atmosphere of carbon monoxide.

*p*-Dimethylaminophenylglyoxylic acid, obtained from the chloride by the action of water, is converted almost quantitatively into *p*-dimethylaminobenzaldehyde when heated with dimethylaniline at 180°.

*Tetramethyl-p*:*p*'-diaminobenzil,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , m. p. 197—198°, forms small, deep yellow crystals, and yields an *osazone*, m. p. 259—260°. C. S.

**Preparation of Substituted Alkylthiolbenzoic Acids.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 212434).—5-Ethoxy-2-methylthiolbenzoic acid,  $\text{EtO} \cdot \text{C}_6\text{H}_3(\text{SMe}) \cdot \text{CO}_2\text{H}$ , m. p. 135°, sparingly soluble in ether, crystallising from dilute alcohol, is prepared from 2-amino-5-hydroxybenzoic acid as follows. The amino-acid (153 parts) is acetylated, treated in alkaline solution with ethyl sulphate (180 parts), and the acetyl group removed with concentrated sodium hydroxide; the liquid acidified, and the amino-group diazotised. The filtered solution is digested at 20—25° with potassium xanthate (180 parts) until the evolution of nitrogen ceases, sodium hydroxide added, the mixture boiled several hours with 300 parts of sodium methyl sulphate (46%), and the product precipitated with mineral acid. 4-Chloro-2-methylthiolbenzoic acid, m. p. 210—211°, sparingly soluble in cold alcohol, ether, or hot water, readily so in hot alcohol, is prepared from 4-chloro-2-aminobenzoic acid by analogous treatment.

4:2-Dimethylthiolbenzoic acid,  $\text{C}_6\text{H}_3(\text{SMe})_2 \cdot \text{CO}_2\text{H}$ , m. p. 194°, easily soluble in hot alcohol, sparingly so in the cold solvent, is obtained when 4-acetyl-amino-2-aminobenzoic acid (from the oxidation and subsequent reduction of 2-nitroaceto-*p*-toluidide) is diazotised and the amino-group replaced by methylthiol as previously described; the acetyl group removed by hydrolysis, and the other amino-group similarly treated. F. M. G. M.

**Preparation of Bromoacetylsalicylic [*o*-Bromoacetyloxybenzoic] Acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 212422).—*o*-Halogenacetyloxybenzoic acids can be prepared by the interaction of the chlorides, bromides, or anhydrides of the bromoparaffin acids with salicylic acid in the presence of a tertiary aromatic amine such as dimethylaniline.

*o*-Bromoacetoxybenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ , prepared by the interaction of salicylic acid and bromoacetyl bromide in presence of dimethylaniline in benzene solution, is a colourless, crystalline powder, m. p. 136—137°, with an acid taste, readily soluble in hot benzene or water, sparingly so in the cold. It is decomposed by prolonged heating with water, and when pure gives no coloration with ferric chloride.

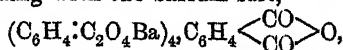
*o*- $\alpha$ -Bromopropionyloxybenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CHMeBr}$ , m. p. 106—107°, has similar properties, and is analogously prepared from  $\alpha$ -bromopropionylbromide.

*o*-Tribromoacetoxybenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CBr}_3$ , m. p. 170—171°, is obtained when tribromoacetyl chloride is employed. These compounds are of therapeutic value. F. M. G. M.

**Barium Salts of Phthalic Acid.** FRANCIS B. ALLAN (*J. Amer. Chem. Soc.*, 1909, 31, 1061—1065).—A study of the barium phthalates has been made by shaking varying quantities of phthalic acid and barium hydroxide with water until equilibrium occurs, and afterwards analysing the solution. It is shown that the four following barium salts exist, the first three of which have been isolated:

$(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4)_3\text{H}_2\text{Ba}\cdot\text{H}_2\text{O}$ ;  
 $\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4\text{Ba}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ ;  
 $(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4\text{Ba})_5\cdot\text{Ba}(\text{OH})_2$ ;  
 $(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4)_5\text{H}_2\text{Ba}_4$ .  
 When the first of these salts is heated at 120—150°, a residue is obtained of the composition  $(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4\text{Ba})_4\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{CO})_2\text{O}$ . The fourth salt differs from this residue only in containing phthalic acid instead of the anhydride. E. G.

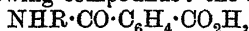
**Third Methyl Ester of Phthalic Acid.** C. G. ALLIN (*J. Amer. Chem. Soc.*, 1909, 31, 1065—1067).—Experiments have been carried out with the view of ascertaining whether a methyl phthalate could be prepared corresponding with the barium salt,



which is obtained by heating the salt,  $(\text{C}_6\text{H}_4\cdot\text{C}_2\text{O}_4)_3\text{H}_2\text{Ba}\cdot\text{H}_2\text{O}$ , at 120—140° (Allan, preceding abstract). When the former salt is heated with methyl sulphate at 100° in a sealed tube for forty-five minutes, a methyl ester,  $\text{C}_6\text{H}_4(\text{CO}_2\text{Me})_2\cdot\frac{1}{4}\text{C}_6\text{H}_4\cdot\text{C}(\text{CO})_2\text{O}$ , m. p. 187°, is obtained, which forms white crystals. The molecular weight was determined by the ebullioscopic method, acetone being used as the solvent. E. G.

**Intramolecular Rearrangement of Phthalamic Acids. IV.** J. BISHOP TINGLE and B. F. PARLETT BRENTON (*J. Amer. Chem. Soc.*, 1909, 31, 1157—1164).—In earlier papers (Tingle and Cram, Abstr.,

1907, i, 692; Tingle and Lovelace, Abstr., 1907, i, 1044; Tingle and Rolker, this vol., i, 28) it has been shown that phthalamic acids,  $\text{NHR} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , are converted by secondary and tertiary amines into imides,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NR}$ , and by primary amines,  $\text{NH}_2\text{R}'$ , into one or more of the following compounds: the amic acid,



the imides,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NR}$  and  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NR}'$ , and the amides,  $\text{NHR} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NHR}'$  and  $\text{C}_6\text{H}_4(\text{CO} \cdot \text{NHR}')_2$ . The investigation has now been extended.

*m*-Nitrophenylphthalamic acid yields normal salts with butylamine, m. p. 169°, isobutylamine, m. p. 182°, isoamylamine, m. p. 172°, benzylamine, m. p. 166°, benzyethylamine, m. p. 169°, and dibenzylamine, m. p. 165°. When heated above the m. p., each of these salts decomposes with liberation of the amine and formation of *m*-nitrophenylphthalimide. A salt could not be obtained with either ammonia, diamylamine, or tribenzylamine.

When the benzylamine salt of *p*-tolylphthalamic acid, m. p. 168°, is heated above its m. p., it is converted into benzyl-*p*-tolylphthalimide,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2\text{Ph}$ , m. p. 153°. Benzylamine  $\beta$ -naphthylphthalamate, m. p. 165°, yields dibenzylphthalimide (Tingle and Lovelace, *loc. cit.*), whilst benzylamine phthalate, m. p. 185°, gives benzylphthalimide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_2\text{Ph}$ , m. p. 116°.

*p*-Chlorophenylphthalamic acid,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 180°, is not changed by prolonged heating with 40% alcohol, but is transformed into *p*-chlorophenylphthalimide by pyridine or aniline at 65°, or by  $\beta$ -naphthylamine at 100°.

Attention has also been directed to phthalamic acids containing two similar or dissimilar groups attached to the nitrogen atom. *Diisobutylphthalamic acid*, m. p. 153°, is not changed when boiled with 40% alcohol or heated with pyridine at 65°; aniline reacts with it at 65° with formation of a small quantity of phenylphthalimide, and  $\beta$ -naphthylamine behaves similarly at 100°, yielding  $\beta$ -naphthylphthalimide.

Pyridine reacts with diphenylphthalamic acid to form pyridine phthalate, m. p. 109°. Aniline transforms this acid into phenylphthalimide, whilst  $\beta$ -naphthylamine converts it into phenylphthalimide and  $\beta$ -naphthylphthalamic acid.

Phenyl- $\beta$ -naphthylphthalamic acid,  $\text{C}_{10}\text{H}_7 \cdot \text{NPh} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 115°, was prepared without difficulty on two occasions, but, for some unexplained reason, could not be obtained subsequently. E. G.

**Dimethylanilinephthalein and Similar Basic Phthaleins.** OTTO FISCHER and FRITZ RÖMME (*Ber.*, 1909, 42, 2934--2938).—Dimethylanilinephthalein, prepared by the fusion of phthalic anhydride, dimethylaniline, and zinc chloride, is obtained as a bluish-green mass which becomes colourless on the addition of water. The colour is ascribed to a partial conversion of the lactonic modification into the quinonoid form. Dimethylanilinephthalein is rendered

greenish-blue by a number of reagents (compare Green, Proc., 1908, 24, 206), including hot acetic acid, phenol, cresol, and 2:4-dinitrophenol. The colour in every case vanishes on dilution with water. The quinonoid esters, which are also greenish-blue, are more stable.

When dimethylanilinephthalein, zinc chloride, and methyl alcohol are heated under pressure at 120—125°, a dark blue mass is obtained; this is dissolved in methyl alcohol, sodium picrate added, and the picrate of methyl malachite-green-o-carboxylate isolated. It crystallises in lustrous, tin-like, columnar crystals from methyl alcohol or in dark olive-green plates from xylene. The same ester is more conveniently prepared by the interaction of methyl dimethylaminobenzophenone-o-carboxylate with dimethylaniline and phosphorus oxychloride.

*Dimethylanilineguaiacolphthalein*, prepared by the condensation of *p*-dimethylaminobenzophenonecarboxylic acid, and guaiacol in presence of 73% sulphuric acid, crystallises in lustrous, glass-like, tabular crystals, m. p. 172—173°. It dissolves in alkalis with a reddish-violet coloration, and gives the reddish-violet coloration of the quinonoid form when warmed with alcoholic zinc chloride. *Dimethylanilinebenzoylguaiacolphthalein* crystallises in colourless needles, m. p. 155—156°.

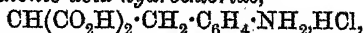
*Dimethylanilinephenolphthalein*, produced in a similar manner by condensation with phenol in presence of 80% sulphuric acid, forms crystals, which become rose-red on exposure to air; m. p. 122—123°.

*Dimethylanilinecatecholphthalein* forms colourless, short columns, m. p. 135°, which dissolves with a violet-red coloration in sodium hydroxide, becoming bluer on dilution. Zinc chloride causes a bluish-red coloration.

*Dimethylaniline-o-cresolphthalein* crystallises in colourless plates, m. p. 110—112°. E. F. A.

**Synthesis of Polypeptides: Derivatives of *p*-Iodophenylalanine.** EMIL ABDERHALDEN and G. ALESSANDRO BROSSA (*Ber.*, 1909, 42, 3411—3416).—The authors have prepared *p*-iodophenylalanine (compare Wheeler and Clapp, Abstr., 1908, i, 981) by the following two methods: (1) *p*-Nitrobenzyl chloride was coupled with ethyl sodiomalonate, the ethyl *p*-nitrobenzylmalonate obtained being reduced and hydrolysed to *p*-aminobenzylmalonic acid, into which an iodine atom was introduced by means of the diazo-reaction. The *p*-iodobenzylmalonic acid was then converted into *p*-iodobenzylbromomalonic acid, and this into *p*-iodophenylbromopropionic acid and *p*-iodophenylalanine successively. (2) From synthetic phenylalanine by way of *p*-nitro- and *p*-amino-phenylalanines. The *p*-iodophenylalanine thus prepared was used in the preparation of glycyl-*p*-iodophenylalanine and diglycyl-*p*-iodophenylalanine.

*p*-Aminobenzylmalonic acid hydrochloride,



has m. p. 178.4° (decomp.), and the free acid, m. p. 213.5° (corr.). When the acid is diazotised and added to cold potassium iodide solution, a crystalline compound, m. p. 192°, separates, which loses nitrogen, yielding *p*-iodobenzylmalonic acid,  $\text{C}_6\text{H}_4\text{I} \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H})_2$ , m. p. 164.4° (corr.).

*Chloroacetyl-p-iodophenylalanine*,  $C_{11}H_{11}O_2NClI$ , crystallises in rhombic leaflets, sinters at  $142\cdot2^\circ$ , and decomposes at  $233\cdot5^\circ$ , m. p.  $160\cdot4^\circ$  (corr.).

*Glycyl-p-iodophenylalanine*,  $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4I$ , crystallises in spherical aggregates of needles, which turn brown at  $250^\circ$ , m. p.  $283^\circ$  (corr.).

*Chloroacetylglycyl-p-iodophenylalanine*,  $C_{13}H_{14}O_4N_2ClI$ , has m. p.  $176\cdot2^\circ$  (corr.).

*Diglycyl-p-iodophenylalanine*,

$NH_2\cdot CH_2\cdot CO\cdot NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4I$ , crystallises in slender needles, m. p.  $240\cdot3^\circ$  (corr.). T. H. P.

**Partial Racemism in Santonin Derivatives.** MARIO LEVI-MALVANO and ANTONIO MANNINO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 144—149).—It has been stated by Ladenburg (this vol., i, 252) that partial racemic compounds, as defined by E. Fischer, have never yet been obtained. The authors point out, however, that such a compound was prepared by Andreocci (Abstr., 1899, i, 931) by crystallising from alcohol a mixture of dextro- and lævo-acetyl-desmotroposantonins (compare also this vol., i, 32).

The authors have examined the following pairs of compounds for the occurrence of partial racemism, the eutectic points being determined for the ternary systems comprising the two active components and a solvent: (1) acetyl-desmotroposantonin and acetyl-*is*-desmotroposantonin in naphthalene; (2) desmotroposantonous and *is*-desmotroposantonous acids in acetanilide and in acetic acid; (3) desmotroposantonous and lævo-desmotroposantonous acids in acetanilide and in acetic acid. The results are as follows:

(1) With these compounds a racemic compound is formed, the eutectic points observed being  $55\cdot9^\circ$  for the racemic compound,  $55^\circ$  for racemic compound + acetyl-desmotroposantonin, and  $54\cdot9^\circ$  for racemic compound + acetyl-*is*-desmotroposantonin; the racemic compound crystallises from alcohol in prisms,  $[\alpha]_D + 108^\circ$ .

(2) With the pair of compounds a partly racemic compound is formed in acetic acid, but not in acetanilide solution at the temperatures employed.

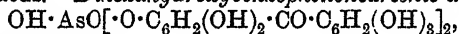
(3) A partly racemic compound is deposited in this case from acetic acid, but not from acetanilide solution.

With *is*-desmotroposantonous and lævo-desmotroposantonous acids, no racemic compound is formed within the limits of the melting-point curve, but in acetanilide these acids yield a partly racemic compound at about  $100^\circ$ . T. H. P.

**Composition and Chemical Constitution of Artificial Tannin.** I. PIETRO BIGINELLI (*Gazzetta*, 1909, 39, ii, 268—283).—When gallic and arsenic acids react in moderately concentrated aqueous solution, and the liquid is evaporated on the water-bath at  $80$ — $90^\circ$ , very little carbon dioxide is liberated, and the reaction proceeds according to one or other of the two following equations, according to the proportions of the two acids employed:  $C_7H_6O_5 + H_3AsO_4 = C_7H_7O_5As + H_2O$ ;  $2C_7H_6O_5 + H_3AsO_4 = C_{14}H_{11}O_{12}As + 2H_2O$ .

The first of these compounds, which the author terms arsenic-gallic acid,  $\text{AsO}(\text{OH})_2 \cdot \text{O} \cdot \text{C} \begin{smallmatrix} \diagup \text{C}(\text{OH}) \cdot \text{CH} \\ \diagdown \text{C}(\text{OH}) \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ , forms a compound with ether (compare Abstr., 1908, i, 40), and is partly hydrolysed in either aqueous or alcoholic solution, this behaviour being in agreement with the observation that hydrogen sulphide effects precipitation of the arsenic in proportions varying with the dilution. The second acid, *arsenic digallic acid*,  $\text{OH} \cdot \text{AsO}[\cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO}_2\text{H}]_2$ , forms a compound with ether and water,  $\text{C}_{14}\text{H}_{11}\text{O}_{12}\text{As} \cdot 13\text{Et}_2\text{O} \cdot 7\text{H}_2\text{O}$ , and probably forms one of the constituents of Schiff's artificial tannin. By dilute acids and even by acetic acid, these compounds are decomposed into gallic and arsenic acids, so that the formation of acetyl derivatives is possible only under special conditions; this behaviour explains the discrepant observations made by Schiff and others on the acetyl derivatives.

When gallic and arsenic acids are heated together in aqueous solution for a number of hours, especially when the proportion of arsenic acid is relatively small, a part of the gallic acid, which at lower temperatures remains unaltered, undergoes transformation into hexahydroxybenzophenone:  $2\text{C}_7\text{H}_6\text{O}_5 - \text{CO}_2 - \text{H}_2\text{O} = \text{C}_{14}\text{H}_{10}\text{O}_7$ . It is found, further, that the arsenic acid and hexahydroxybenzophenone react to give compounds, which may also be obtained from the corresponding gallic acid derivatives by heating their solutions for some time in a reflux apparatus. *Dihexahydroxybenzophenonearsenic acid*,



was obtained in this way.

Pyrogallol also reacts with arsenic acid, yielding *dipyrogallolarsenic acid*,  $\text{OH} \cdot \text{AsO}[\cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OH})_2]_2$ , which is an amorphous compound, violet and hygroscopic when separated from ethereal solution, and green when deposited from water; it combines with 1 mol. of ether.

It is evident that, for the formation of an artificial tannin by the action of arsenic acid, the presence of a carboxyl group in the compound is unnecessary, three hydroxyl groups in the positions 1:2:3 being sufficient.

The results of Schiff and others are discussed.

T. H. P.

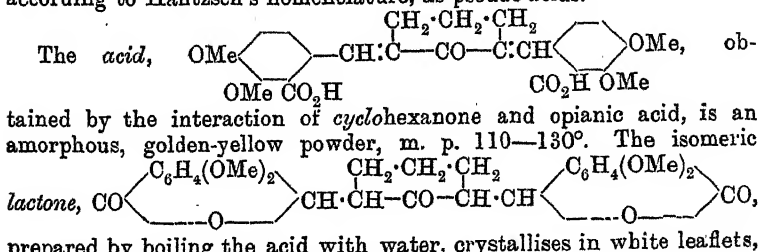
**Artificial Tannin. II.** PIETRO BIGINELLI (*Gazzetta*, 1909, 39, ii, 283—289. Compare preceding abstract).—Compounds similar to those described in the preceding paper are given by the action of phosphoryl chloride or antimonious acid on gallic acid, the reactions being expressed by the following equations:  $3\text{C}_7\text{H}_6\text{O}_5 + \text{POCl}_3 = 3\text{HCl} + \text{PO}[\cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2(\text{CO}_2\text{H})]_3$  and either  $\text{C}_7\text{H}_6\text{O}_5 + \text{H}_3\text{SbO}_4 = \text{SbO}(\text{OH})_2 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$  or  $2\text{C}_7\text{H}_6\text{O}_5 + \text{H}_3\text{SbO}_4 = \text{CH} \cdot \text{SbO}[\cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CO}_2\text{H}]_2 + 2\text{H}_2\text{O}$ , according to the proportions of the reacting acids. With pyrogallol, antimonious acid yields the compound,  $\text{OH} \cdot \text{SbO}[\cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OH})_2]_2$ , analogous to dipyrogallolarsenic acid. The compound  $\text{PO}(\text{C}_7\text{H}_5\text{O})_3$  combines with  $3\text{Et}_2\text{O}$ , and the compound  $\text{SbO}(\text{C}_7\text{H}_7\text{O}_7)$  with  $1\text{Et}_2\text{O}$ . Antimonious acid does not react, under the conditions employed, with phloroglucinol or quinol.

T. H. P.

**Preparation of Salicylosalicylic [*o*-Salicyloxybenzoic] Acid.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 211403).—*Salicylosalicylic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , m. p. 147–148°, sparingly soluble in cold alcohol or ether, is obtained when the organic salicylates are treated in an organic solvent with condensing agents, such as phosphorus trichloride, phosphoryl chloride, carbonyl chloride, or thionyl chloride. Salicylic acid (5 parts) and dimethylaniline (5.2 parts) in benzene (1.5 parts) are cooled, and a mixture of phosphorus trichloride (1 part) and benzene (1.5 parts) slowly added. The mixture is left for several days at the ordinary temperature, then acidified with hydrochloric acid, and the unchanged salicylic acid separated with hot water. The product is crystalline, tasteless, and has no irritating action on the stomach, but is rapidly hydrolysed in the intestines.

F. M. G. M.

**Condensation of Opianic and Phthalaldehydic Acids with *cyclo*Hexanone and Diethyl Ketone.** OTTO MORGENSTERN (*Monatsh.*, 1909, 30, 681–693).—The author has studied the condensation of the symmetrical ketones, *cyclo*hexanone and diethyl ketone, with opianic and phthalaldehydic acids. In the condensations with *cyclo*hexanone, the latter reacts with both the methylene groups adjacent to the carbonyl group, yielding the acids  $\text{C}_{26}\text{H}_{26}\text{O}_9$  and  $\text{C}_{22}\text{H}_{18}\text{O}_5$ , which were transformed into the lactones isomeric with them. These results are in accord with those obtained by Vorländer and Hobohm (Abstr., 1896, i, 603) in studying the action of benzaldehyde on *cyclo*hexanone. The condensation products of *cyclo*hexanone with opianic and phthalaldehydic acids are stable at the ordinary temperature, whilst those formed by non-cyclic ketones readily undergo change into the corresponding lactones. The action of diethyl ketone on opianic and phthalaldehydic acids is similar to that of the other non-cyclic ketones previously studied (compare Hamburger, Abstr., 1899, i, 142; Goldschmidt and Knöpfer, Abstr., 1900, i, 35; Fulda, Abstr., 1900, i, 36). When titrated with alcoholic alkali hydroxide, all the lactones obtained by the author undergo more or less gradual neutralisation; they must therefore be regarded, according to Hantzsch's nomenclature, as pseudo-acids.



prepared by boiling the acid with water, crystallises in white leaflets, m. p. 196–197°, and forms a yellow *potassium* salt,  $\text{C}_{26}\text{H}_{24}\text{O}_9\text{K}_2$ , and a *methyl* ester,  $\text{C}_{28}\text{H}_{30}\text{O}_9$ , m. p. 184–186°, which takes up less bromine than corresponds with the compound  $\text{C}_{28}\text{H}_{30}\text{O}_9\text{Br}_4$ . The compounds formed by the lactone with hydroxylamine hydrochloride, hydroxylamine in alkaline solution, and phenylhydrazine could not be obtained pure.

The compound,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2)\cdot\text{CO}\cdot\text{C}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2)\cdot\text{CO}_2\text{H}$ , formed by cyclohexanone and phthalaldehydic acid, separates in pale brown flocks, and, on boiling with water, is converted into (1) the isomeric lactone,  $\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}$ , which forms white crystals, m. p. 205–206°, and (2) the lactone,  $\text{C}_{44}\text{H}_{34}\text{O}_9$ , formed by condensation of 2 mols. of the normal lactone with loss of  $\text{H}_2\text{O}$ , which is a white, amorphous powder and unites with less than 2Br.

The acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{C}(\text{OMe})\cdot\text{COEt}$ , formed by the interaction of phthalaldehydic acid (1 mol.) and diethyl ketone (1 mol.) in presence of sodium hydroxide, readily changes into the corresponding lactone,  $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{CHMe}\cdot\text{COEt}$ , m. p. 109°, which forms a colourless potassium salt. Another lactone,  $\text{C}_{45}\text{H}_{40}\text{O}_{10}$ , which accompanies the above and is more readily obtained by using 2 mols. of phthalaldehydic acid to 1 mol. of ketone, forms colourless crystals, m. p. 205–207°, and has the normal molecular weight in boiling benzene.

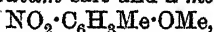
Condensation of opianic acid (1 mol. or 2 mols.) and diethyl ketone (1 mol.) yields a yellow resin, from which no definite compound could be isolated. T. H. P.

**General Reaction of Aldehydes and Ketones.** HARTWIG FRANZEN (*Ber.*, 1909, 42, 3293–3295).—Benzaldehyde, when shaken with an aqueous solution of calcium cyanide, yields the calcium derivative of mandelonitrile,  $(\text{CN}\cdot\text{CHPh}\cdot\text{O})_2\text{Ca}$ . Similar compounds have been prepared by treating salicylaldehyde, *m*-nitrobenzaldehyde, cuminaldehyde, *p*-methylbenzaldehyde, formaldehyde, heptaldehyde, acetone, ethyl acetoacetate, ethyl benzoylacetate, acetylacetone, and acetonylacetone with the cyanides of calcium, strontium, barium, and magnesium. Acetophenone does not appear to form a solid compound with calcium cyanide.

The calcium derivative of mandelonitrile is a fine pale orange-yellow powder, having a slight odour of hydrogen cyanide. It is decomposed by boiling water, but not quantitatively, into calcium cyanide and benzaldehyde. W. H. G.

**4-Amino-3-methoxybenzaldehyde.** EUGEN KHOTINSKY and W. JACOPSON-JACOPMANN (*Ber.*, 1909, 42, 3097–3103).—The authors have not been able to obtain pure vanillin from 4-amino-3-methoxybenzaldehyde (compare Tiemann and Ludwig, *Abstr.*, 1883, 189; Ulrich, *ibid.*, 1886, 60). The aldehyde was prepared by Geigy's method (D.R.-P. 86874).

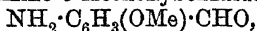
When *m*-cresol is nitrated by Staedel's method (*Abstr.*, 1889, 497; 1891, 186), a mixture of three mononitro-derivatives is obtained. The 6-nitro-derivative is not volatile in steam, whereas the 4- and 2-nitro-compounds are both volatile, but can be separated readily, as the 2-derivative is soluble in water and may be extracted by ether. It forms an intensely red sodium salt and a methyl ether,



in the form of colourless crystals, m. p. 88–89°.

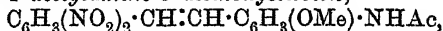
The best yield of 4-nitro-*m*-cresol is obtained when the nitration is conducted at  $-8$  to  $-5^{\circ}$ . Only small amounts of the 4-nitro-compound are formed when Denningèr's (Abstr., 1890, 38) or Noelting and Wild's (Abstr., 1885, 973) method is used. In both cases the 6- and 2-nitro-compounds are the chief products.

4-Nitro-*m*-tolyl methyl ether,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}$ , obtained by the action of methyl sulphate on sodium 4-nitro-*m*-cresol, forms colourless crystals, m. p.  $62^{\circ}$ . When treated with sulphur and alcoholic sodium hydroxide, it yields 4-amino-3-methoxybenzaldehyde,



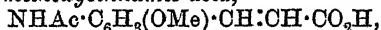
m. p.  $102^{\circ}$ , which is not volatile in steam. When diazotised and coupled with an alkaline solution of  $\beta$ -naphthol, it yields an *azo-dye*,  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2$ , m. p.  $212^{\circ}$ . The *acetyl* derivative,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$ , has m. p.  $147^{\circ}$ . The *oxime*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} : \text{N} \cdot \text{OH}$ , crystallises from alcohol, and has m. p.  $142^{\circ}$ ; it yields an *azo-dye*,  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_3\text{Na}$ , m. p.  $229-230^{\circ}$ .

2 : 4-Dinitro-4'-acetylamino-3'-methoxystilbene,



obtained by condensing the acetylamino-aldehyde with 2 : 4-dinitrotoluene in the presence of piperidine, crystallises from nitrobenzene in brownish-red prisms, m. p.  $227^{\circ}$ . The corresponding *amino*-compound, obtained by hydrolysis of the acetyl derivative with alcoholic hydrochloric acid, crystallises from nitrobenzene and yields an *azo-dye*,  $\text{C}_{25}\text{H}_{17}\text{O}_6\text{N}_4\text{Na}$ , m. p.  $239^{\circ}$ , and soluble in sulphuric acid to blue solutions.

4-Acetylamino-3-methoxycinnamic acid,



obtained by Perkin's condensation from the acetylamino-aldehyde, crystallises from alcohol, and has m. p.  $100^{\circ}$ .

4-Amino-*m*-tolyl methyl ether,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}$ , obtained as a by-product in the preparation of the amino-aldehyde, has b. p.  $237-239^{\circ}$ . The *acetyl* derivative,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}$ , has m. p.  $131^{\circ}$ , and the *azo-dye*,  $\text{C}_{18}\text{H}_{16}\text{O}_2\text{N}_2$ , obtained by diazotising the amino-methyl ether and coupling with  $\beta$ -naphthol, has m. p.  $173^{\circ}$ . J. J. S.

**Isomerism of Anils (Schiff's Bases).** WILHELM MANCHOT and J. R. FURLONG (*Ber.*, 1909, 42, 3030-3036).—The anils formed by the condensation of aromatic aldehydes with primary aromatic amines should, according to the Hantzsch-Werner theory, exist in two isomeric forms. The existence of these two forms is at present doubtful, the best recorded instance being that of the product from aniline and *p*-homosalicylaldehyde (Anselmino, Abstr., 1907, i, 913). It is, however, doubtful whether this is occasioned by chemical isomerism or physical polymorphism.

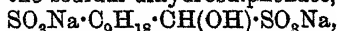
The anil from salicylaldehyde and ethyl *p*-aminobenzoate exists in yellow and red modifications. The yellow form is obtained by mixing concentrated alcoholic solutions of the components and quick crystallisation; the red form, on the other hand, results from the slow crystallisation of dilute solutions. The yellow form consists of flat, hexagonal plates, single crystals being colourless; the red modification forms long, prismatic crystals with rectangularly cut ends. The yellow

form melts when quickly heated at  $87.5^\circ$ , the red at  $83^\circ$  without becoming properly liquid; it then becomes yellow, and has m. p.  $87.5^\circ$ .

The yellow isomeride is the primary form, and the only one obtainable by direct synthesis. The red isomeride can only be obtained by rearrangement from the yellow form. Accordingly, they are regarded as different chemically. They have the same composition, but differ in solubility.

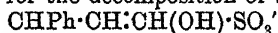
E. F. A.

**Combined Sulphurous Acids. IV and V.** WILHELM KERP and P. WÖHLER (*Arb. Kais. Ges. Amt.*, 1909, 32, 89—143. Compare *Abstr.*, 1904, i, 713; 1907, i, 1010, 1012).—The behaviour of the three types of salts formed by combination of the unsaturated aldehydes, citronellal and cinnamaldehyde, with sulphurous acid or sodium hydrogen sulphite has been investigated in aqueous solution. In the case of citronellal, the compounds in question are (1) the normal bisulphite compound,  $C_9H_{17}\cdot CH(OH)\cdot SO_3Na$ , the sodium hydrosulphonate,  $SO_3Na\cdot OMe_2\cdot [CH_2]_3\cdot CHMe\cdot CH_2\cdot COH$ , formed by addition at the double linking, and the sodium dihydrosulphonate,



formed by addition in both positions. These compounds have already been described by Tiemann (*Abstr.*, 1899, i, 248).

The normal bisulphite compounds do not reach a definite equilibrium when acted on by water, as the bisulphite ion reacts with some of the normal bisulphite compound to form the sodium dihydrosulphonate ion. As, however, the first action is rapid in comparison with the second, it is possible to measure the speed of both reactions, and this has been done for the cinnamaldehyde compounds. The rate of decomposition of the citronellal complex could not be determined, owing to the fact that citronellal accelerates the oxidation of sulphurous acid by the oxygen of the air, a process which disturbs the measurements. The constant for the decomposition of the



ion is  $1.02 \times 10^{-3}$  at  $25^\circ$ .

The dihydrosulphonates of the two aldehydes lose sulphurous acid from the aldehyde group in the normal way in aqueous solution, but the amount lost is much less than in the case of the normal bisulphite compounds. The constant for the citronellal compound is  $0.8 \times 10^{-6}$ , and for the cinnamaldehyde compound  $4.06 \times 10^{-6}$ . Hence the addition of bisulphite at the double bond greatly diminishes the tendency for it to be eliminated from the aldehyde group. As may be anticipated, the compound  $SO_3Na\cdot C_9H_{17}\cdot COH$  is stable in aqueous solution. The pharmacological action of the complex sulphurous acids is discussed in the light of these results.

The bisulphite compound with furfuraldehyde has also been prepared, and its behaviour in aqueous solution examined. The average value of the constant, obtained by experiments in  $N/1$ ,  $N/10$ , and  $N/30$  molar aqueous solution, is  $0.72 \times 10^{-3}$ . The equilibrium is established almost instantaneously in aqueous solution, but much more slowly in acid solution, and, in the latter case, the amount of decomposition is greater. This is doubtless owing to the presence of the non-ionised furfuraldehydesulphurous acid, which is decomposed to a greater extent

than the anion. Furfuraldehyde does not combine with sulphurous acid at the double linking.

The mode of occurrence of sulphurous acid in the residual solution obtained in the extraction of cellulose from wood by means of sulphurous acid has been investigated. G. S.

*p*-Benzoyltriphenylmethane and *p*-Benzoyldiphenylmethane. *p*-Benzoyltriphenylcarbinol and Benzoylbenzophenone. MAURICE DELACRE (*Bull. Soc. chim.*, 1909, [iv], 5, 952—958, 958—962).—Bourcet has prepared *p*-benzoyltriphenylmethane by condensing benzene with phenyl  $\omega$ -dibromo-*p*-tolyl ketone (Abstr., 1897, i, 566), and this method of preparation has been confirmed by Schmidlin (Abstr., 1907, i, 26, 601). The author has repeated this work and obtained somewhat different results. Three products result from the condensation: (1) a hydrocarbon of about  $C_{14}$  complexity, boiling at  $240^\circ$ ; (2) *p*-benzoyldiphenylmethane, and (3) *p*-benzoyltriphenylmethane.

The last-mentioned substance occurs in two forms, the one in vitreous crystals, the other in silky spangles, both of which melt at  $161^\circ$ , as against  $164^\circ$  recorded by Bourcet (*loc. cit.*), but show slight differences in solubility. A mixture of both forms, obtained by crystallising from acetic acid, gradually changes wholly into the spangle form. On oxidation with chromic acid, *p*-benzoyltriphenylmethane yields *p*-benzoyltriphenylcarbinol, which crystallises either with 1 mol. of acetic acid, and then melts at  $80^\circ$ , or anhydrous, and then has m. p.  $116^\circ$  (not  $157^\circ$  as stated by Bourcet, *loc. cit.*). By the further action of the oxidising agent on the carbinol, some *p*-benzoylbenzophenone is formed. The latter is also produced by the oxidation of benzoyldiphenylmethane, obtained as described above. T. A. H.

Nature of Quinhydrones and Triphenylmethane Dyes. WILHELM SCHLENK [with ANGELO KNORR] (*Annalen*, 1909, 368, 277—295).—I. *New Types of Quinhydrone-like Compounds.*—*p*-Benzoquinone and its tetrachloro-derivative unite with quinol dimethyl ether when melted together, forming brownish-red and intensely violet-blue quinhydrone-like compounds respectively, which are so unstable that they dissociate into their components at the ordinary temperature.

*p*-Benzoquinonedi-imine and benzidine combine in ethereal solution, forming the *quinhydrone-base*,  $C_6H_4(NH)_2.C_{12}H_8(NH_2)_2$ , which crystallises in long, ruby-red needles, commences to decompose at about  $128^\circ$ , and is completely molten at  $145^\circ$ .

The following quinone-diamines are prepared by bringing the components together in a suitable solvent; with the exception of the compound from *p*-benzoquinone and *p*-phenylenediamine, they contain the components in equimolecular proportions.

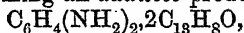
Tetrachloro-*p*-benzoquinone forms *quinone-diamines* with the following bases: (1) *p*-phenylenediamine, bluish-black, glistening needles; (2) tetramethyl-*p*-phenylenediamine, glistening, dark red needles with a bronzy reflex, m. p. about  $80^\circ$ ; (3) 3:3'-dibromo-*o*-tolidine, bluish-black needles, m. p.  $225$ — $228^\circ$ ; (4) 3:3'-dichloro-*o*-tolidine, black,

glistening needles; (5) tetramethylbenzidine, nodules of violet-black, hexagonal leaflets.

Tetrabromo-*p*-benzoquinone forms *quinone-diamines* with 3:3'-dibromo-*o*-tolidine, greenish-black, glistening needles, m. p. 190°, and with tetramethylbenzidine, violet-black leaflets.

The *quinone-diamine*,  $5C_6H_4O_2 \cdot 2C_6H_4(NH_2)_2$ , obtained from *p*-benzoquinone and *p*-phenylenediamine, forms dark blue crystals, m. p. about 83°.

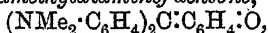
Fluorenone, having a semi-quinonoid structure, combines with *p*-phenylenediamine, forming an *additive* product,



which crystallises in small, brick-red needles, and with benzidine, yielding the *additive* product,  $C_{12}H_8(NH_2)_2 \cdot 2C_{13}H_8O$ , which crystallises in glistening, yellow prisms and slender leaflets, m. p. 126—127°.

II. *Constitution of Quinhydrone-like Compounds*.—This part of the paper is mainly polemical against Willstätter and Piccard (Abstr., 1908, i, 475). The formulæ assigned by these authors to Wurster's dye salts and quinhydrone are considered very improbable, for many complex partial-quinonoid immonium salts, likewise the quinhydrone-like *additive* product of 2 mols. of *p*-phenylenediamine with 5 mols. of *p*-benzoquinone, cannot be formulated in the same manner. The quinhydrones and similar compounds are *additive* products, which at present cannot be represented by structural formulæ.

III. *Constitution of Triphenylmethane Dyes*.—The theories advanced by von Baeyer (Abstr., 1907, i, 757) and by Willstätter and Piccard (*loc. cit.*) to account for the colour of triphenylmethane dyes are improbable, since *tetramethyldiaminofuchsons*,



is as intensely coloured as magenta. It crystallises in brick-red prisms, and is prepared by condensing Michler's ketone by Grignard's method with *p*-iodoanisole and removing the methoxy-group from the methoxy-malachite green thus formed by means of a mixture of glacial acetic acid and 60% sulphuric acid. W. H. G.

**Quinonoid Derivatives of Diphenyl.** II. WILHELM SCHLENK [with HUGO KELLER and ANGELO KNORR] (*Annalen*, 1909, 368, 271—277).—*Quinonechloroimines*.—In continuation of the investigation recorded previously (this vol., i, 36), it is shown that an analogy exists between the 1:2-positions in benzene and the 2:2'-positions in diphenyl, since 2:2'-diaminodiphenyl when treated with hydrochloric acid and sodium hypochlorite in dilute aqueous solutions yields 2:2'-*diphenquinonedichlorodi-imine*,  $C_{12}H_8N_2Cl_2$ , a chocolate-brown, amorphous powder, which explodes slightly when heated. 2:4'-*Diphenquinonedichlorodi-imine*,  $C_{12}H_8N_2Cl_2$ , prepared by the same method from the corresponding diamine, is a light brown, amorphous powder, which explodes slightly when heated.

*Partial-quinonoid Immonium Salts*.—The term *partial-quinonoid* ("theilchinoid") is employed instead of *meri-quinonoid*, since the author cannot agree with the views of Willstätter and Piccard (compare Abstr., 1908, i, 915) associated with this term.

It is found that derivatives of benzidine having only weakly basic

properties, such as 2 : 2'-dinitrobenzidine, 3 : 3'-dinitrobenzidine, 4 : 4'-dinitro-*o*-tolidine, and diacetylbenzidine, do not yield partial-quinonoid salts when oxidised. Further, as a general rule, only those benzidine bases yield partial-quinonoid salts which give rise to substantive, cotton azo-dyes.

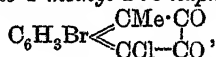
*Coerulignone*.—It is shown by titration with stannous chloride that, contrary to the statement of Moir (Proc., 1906, 22, 110), *coerulignone* (*cedrilet*) is a quinone and not a quinhydrone. W. H. G.

The Constitution of Thiophenoquinone. THEODOR POSNER (*J. pr. Chem.*, 1909, [ii], 80, 270—282).—Polemical. A reply to Michael (this vol., i, 494). J. V. E.

2 : 3-Quinone of 1-Methylnaphthalene. KARL FRIES and J. EMPSON (*Ber.*, 1909, 42, 3375—3381).—4-Chloro-6-bromo-3-hydroxy-1-methyl-2-naphthaquinone,  $C_6H_3Br \begin{smallmatrix} CMe(NO_2) \cdot CO \\ CCl \text{ --- } C \cdot OH \end{smallmatrix}$ , prepared by the action of nitrous acid on 4-chloro-6-bromo-2 : 3-dihydroxy-1-methylnaphthalene (see following abstract), crystallises from benzene in nodular masses, m. p. 110—112° (decomp.).

4-Chloro-6-bromo-1 : 2-dinitro-2 : 2 : 3 : 3-tetrahydroxy-1-methylnaphthalene,  $C_6H_3Br \begin{smallmatrix} CMe(NO_2) \cdot C(OH)_2 \\ CCl(NO_2) - C(OH)_2 \end{smallmatrix}$ , prepared by the action of nitric acid on 4-chloro-6-bromo-2 : 3-dihydroxy-1-methylnaphthalene (compare Zincke and Fries, *Abstr.*, 1904, i, 1008), forms white crystals, m. p. 102° (decomp.).

The action of iodine on the lead salt of 4-chloro-6-bromo-2 : 3-dihydroxy-1-methylnaphthalene gives a yellow, amorphous compound,  $(C_{11}H_6O_2ClBr)_3$ , m. p. 210°, which, when heated in acetic acid solution, gives 4-chloro-6-bromo-1-methyl-2 : 3-naphthaquinone,



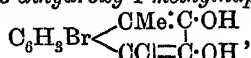
which crystallises from acetic acid in rosettes of yellow prisms or flat needles decomposing at about 220°, and has the theoretical molecular weight in boiling ethyl acetate and double this value in boiling benzene. Treatment of this compound with *o*-phenylenediamine in alcohol or benzene yields 6-chloro-8-bromo-11-methyl- $\beta\beta$ -naphtha-phenazine (see following abstract). T. H. P.

2 : 3-Diketo-derivative of Tetrahydro-1-methylnaphthalene. KARL FRIES and ERNST HEMPELMANN (*Ber.*, 1909, 42, 3381—3388. Compare preceding abstract).—A better method for the reduction of 6-bromo-3-nitro-1 : 2-methylnaphtha- $\psi$ -quinol (compare Fries and Hübner, *Abstr.*, 1906, i, 190) to 6-bromo-3-amino-1-methyl- $\beta$ -naphthol is by means of stannous chloride in presence of hydrochloric and acetic acids.

1 : 4 : 4-Trichloro-6-bromo-2 : 3-diketo-1-methyltetrahydronaphthalene,  $C_6H_3Br \begin{smallmatrix} CClMe \cdot CO \\ CCl_2 - CO \end{smallmatrix}$ , prepared by chlorinating 6-bromo-3-amino-1-

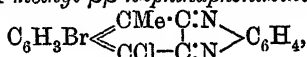
methyl- $\beta$ -naphthol, separates in nodular crystals, m. p. 132—138° (decomp.).

4-Chloro-6-bromo-2:3-dihydroxy-1-methylnaphthalene,



obtained on reducing the preceding compound, crystallises in slender, silky needles, m. p. 184°, and in alcoholic or acetic acid solution gives a deep blue coloration with ferric chloride; its diacetyl derivative has m. p. 184°.

6-Chloro-8-bromo-11-methyl- $\beta\beta$ -naphthaphenazine,

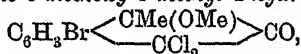


prepared from 1:4:4-trichloro-6-bromo-1-methyl-2:3-diketotetrahydronaphthalene and *o*-phenylenediamine, separates in slender, carmine-red needles, decomposing at 230—270°.

The action of calcium hypochlorite on 1:4:4-trichloro-6-bromo-2:3-diketo-1-methyltetrahydronaphthalene yields (1) 1:3:3-trichloro-5-bromo-1-methyl-2-hydrindone,  $\text{C}_6\text{H}_3\text{Br} \begin{array}{c} \text{CMeCl} \\ \diagup \quad \diagdown \\ \text{CCl}_2 \end{array} > \text{CO}$ , which crystallises in thick plates, m. p. 75°; (2) 4-bromo-1-methylphthalide-1-carboxylic acid,  $\text{C}_6\text{H}_3\text{Br} \begin{array}{c} \text{CMe}(\text{CO}_2\text{H}) \\ \diagup \quad \diagdown \\ \text{CO} \end{array} > \text{O}$ , which crystallises in small prisms, m. p. 132—135°.

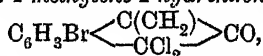
4-Bromo-1-methylphthalide,  $\text{C}_6\text{H}_3\text{Br} \begin{array}{c} \text{CHMe} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} > \text{O}$ , obtained by heating the preceding compound at 200°, crystallises in long prisms, m. p. 62°.

3:3-Dichloro-5-bromo-1-methoxy-1-methyl-2-hydrindone,



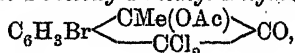
prepared by the action of sodium methoxide on 1:3:3-trichloro-5-bromo-1-methyl-2-hydrindone, is very unstable and forms small, shining scales, m. p. 108°.

3:3-Dichloro-5-bromo-1-methylene-2-hydrindone,



separates from an acetic acid solution of the preceding compound and crystallises in faintly yellow prisms, m. p. 200°.

3:3-Dichloro-5-bromo-1-acetoxy-1-methyl-2-hydrindone,



separated from the acetic acid mother liquor from the preceding compound, crystallises in thin plates, m. p. 126—133°. T. H. P.

**Preparation of Acetylaminanthraquinones.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 211958).—Aminoanthraquinones can be readily acetylated in the presence of fuming sulphuric acid (23%  $\text{SO}_3$ ). Aminoanthraquinone (10 parts) is dissolved in 100 parts of fuming sulphuric acid, and acetic anhydride (10 parts) stirred in, the temperature being maintained at 30—40° until the reaction is complete; this is indicated by the formation of a yellow precipitate on the addition of water, and the absence of a red coloration. F. M. G. M.

**Side-Chain Halogen Substituted Methylanthraquinone.** MAX H. ISLER (*J. pr. Chem.*, 1909, [ii], 80, 287—288. Compare this vol., i, 563).—In criticising the recent publication of Otto Fischer (*loc. cit.*), numerous references unmentioned by this author are given to previously published work on the preparation of methylanthraquinones in which halogen is a substituent in the side-chain.

The opinion is expressed that Fischer's  $\omega$ -substituted methylanthraquinone is probably a ring substituted methylanthraquinone.

J. V. E.

**Preparation of 1:2-Dihydroxyanthraquinone-3:5- and 3:8-disulphonic Acids.** R. WEDEKIND & Co. (D.R.-P. 210863. Compare this vol., i, 496).—By the sulphonation of alizarin-3-sulphonic acid in presence of mercury, the same two disulphonic acids are produced as are formed by sulphonating alizarin directly in presence of mercury. The latter are therefore the 3:5- and the 3:8-disulphonic acids. It is not necessary first to isolate the alizarin-3-sulphonic acid for their preparation, but when the formation of the monosulphonic acid is complete, mercury is added to the sulphonation mixture, which is then further heated. The salts of the 3:5-acid are more sparingly soluble than those of the 3:8-compound.

With dilute sulphuric acid at  $170^{\circ}$ , the sulphonic group in position 3 is eliminated, and 1:2-dihydroxyanthraquinone-5- and -8-sulphonic acids are formed. 1:2:5-Trihydroxyanthraquinone has m. p.  $278^{\circ}$ , and 1:2:8-trihydroxyanthraquinone, m. p.  $239$ — $240^{\circ}$ , instead of  $272$ — $274^{\circ}$  and  $230^{\circ}$  respectively as previously recorded.

F. M. G. M.

**The Resolution of *d,l*-Camphorsulphonic Acid into its Optically Active Components.** BRUNO REWALD (*Ber.*, 1909, 42, 3136—3138).—This resolution of the camphorsulphonic acid prepared from synthetic camphor furnishes an additional argument for the view that the latter is the racemic form of the natural product. The resolution was effected by means of brucine. Brucine *d*-camphorsulphonate first separates in aggregations of rhombohedral crystals; the *l*-salt is more soluble, and forms small needles. From the salts, the free acids were obtained by decomposing with baryta. *d*-Camphorsulphonic acid, m. p.  $193$ — $195^{\circ}$  (decomp.), has (in agreement with Reychler's value for the acid from natural camphor)  $[\alpha]_D^{20} + 22.06^{\circ}$ . The rotation of the acid from pure *d*-camphor was determined afresh, and found to be  $[\alpha]_D^{20} + 22.60^{\circ}$ .

1-Camphorsulphonic acid has m. p.  $193$ — $195^{\circ}$  (decomp.);  $[\alpha]_D^{20} - 20.75^{\circ}$ .

R. V. S.

**Terpenes and Ethereal Oils.** CI. OTTO WALLACH (*Annalen*, 1909, 369, 63—103. Compare this vol. i., 726).—I. *The Fenchone Series*.—The author's formula for fenchone is finally abandoned, since the reactions described in this communication cannot be explained by its aid. It is possible by making use of Semmler's formula to deduce structural formulæ for the compounds described later, but these are by no means definitely established.

[With HEINRICH WIENHAUS.]—Contrary to Semmler's statement

(compare Abstr., 1908, i, 37), fenchone reacts as completely, although not so readily, with sodium as camphor. The chief product of the reaction is the pinacone of fenchone,  $C_{20}H_{34}O_2$ , which has been described previously (Abstr., 1898, i, 486); it has b. p.  $219-220^\circ/13$  mm., and crystallises in stout prisms and plates, m. p.  $97^\circ$ , and in slender needles, m. p.  $94^\circ$ . The pinacone from *d*-fenchone has  $[\alpha]_D^{15} + 45.00^\circ$  (in ethyl acetate),  $+ 32.26^\circ$  (in benzene),  $[\alpha]_D^{20} + 32.08^\circ$  (in benzene); the pinacone from *l*-fenchone has  $[\alpha]_D^{20} - 44.78^\circ$  (in ethyl acetate),  $- 36.70^\circ$  (in benzene); the *racemic* compound has m. p.  $104-105^\circ$ . If air be not excluded during the reaction, an *acid*, which dissolves in aqueous alkalis to a yellowish-red solution, and small quantities of fencholic acid are formed.

Fencholic acid is identical with Semmler's dihydrofencholenic acid (b) (compare Abstr., 1906, i, 681), but is so named in order to emphasise its analogy to campholic acid. It is readily prepared by heating fenchone with solid potassium hydroxide under pressure at  $220-240^\circ$ ; the product obtained thus is a mixture of two isomerides, one of which is present, however, in extremely small quantities; it forms large, hard crystals, m. p.  $18-19^\circ$ , b. p.  $255-256^\circ/760$  mm.;  $151-152^\circ/17$  mm.,  $D_{20}^{20} 0.9700$ ,  $n_D^{20} 1.4563$ ,  $n_D$  (in 1-dm. tube)  $+ 3.92^\circ$  to  $+ 4.28^\circ$ . The *chloride*,  $C_9H_{17}COCl$ , obtained by the action of phosphorus trichloride on the acid, has b. p.  $100/15$  mm.,  $218-219^\circ/750$  mm.,  $D_{20}^{20} 1.0045$ ,  $n_D^{20} 1.4606$ ,  $[\alpha]_D^{19} - 2.43^\circ$ ; the following compounds are obtained from it by the usual methods: ethyl fencholate, a colourless liquid with a fruity odour, b. p.  $222-223^\circ$ ,  $D_{19}^{19} 0.913$ ,  $n_D^{19} 1.4392$ ; *isoamyl fencholate*,  $C_{15}H_{28}O_2$ , a colourless liquid, b. p.  $262-269^\circ$ ,  $D_{19}^{19} 0.903$ ,  $n_D^{19} 1.4436$ ; *fencholanilide*,  $C_9H_{17}CO \cdot NHPh$ , large prisms, m. p.  $79-80^\circ$ .

[With FRIEDRICH RITTER.]—When fencholamide (1 mol.) is acted on by bromine (1 mol.) and subsequently treated with an aqueous solution of potassium hydroxide (2 mols.), it yields *fenchelylcarbimide*,  $C_9H_{17}N \cdot CO$ , a slightly yellow oil, b. p.  $201^\circ$ ,  $[\alpha]_D^{19} + 3.04^\circ$ ,  $D_{19}^{19} 0.9210$ ,  $n_D^{19} 1.4461$  (compare Bouveault and Levallois, Abstr., 1908, i, 193). The carbimide reacts (1) with ammonia, forming *fenchelylcarbamide*,  $NH_2 \cdot CO \cdot NH \cdot C_9H_{17}$ , m. p.  $129-130^\circ$ ; (2) with fenchelylamine, yielding difenchelylcarbamide, m. p.  $169^\circ$  (compare Bouveault and Levallois, *loc. cit.*); (3) with piperidine, yielding the *carbamide* derivative,  $C_5H_{10}N \cdot CO \cdot NH \cdot C_9H_{17}$ , colourless needles, m. p.  $96^\circ$ .

*Fenchelylamine*,  $C_9H_{17}NH_2$ , prepared by hydrolysing the carbimide with hot concentrated hydrochloric acid, is a colourless, limpid liquid, b. p.  $173^\circ$ ,  $D_{20}^{20} 0.832$ ,  $n_D^{20} 0.4450$ , which absorbs carbon dioxide readily, and forms a *hydrochloride*, m. p.  $169-170^\circ$ ,  $[\alpha]_D + 2.95^\circ$  (in water), and a *platinichloride* crystallising in leaflets. The hydrochloride decomposes when heated, yielding a hydrocarbon,  $C_9H_{16}$ , which is also formed together with other hydrocarbons by the dry distillation of sodium fencholate, and is identical with that described by Bouveault and Levallois (*loc. cit.*). The hydrocarbon yields a crystalline *nitrosochloride*,  $(C_9H_{16}NOCl)_2$ , m. p.  $115^\circ$ , which when acted on by piperidine yields the crystalline *nitrolpiperidide*,  $C_9H_{16}NO \cdot C_5NH_{10}$ , m. p.  $159-159^\circ$ . A *ketone*,  $C_9H_{14}O$ , is obtained by hydrolysing the oily *oxime* which results from the action of sodium acetate on the nitrosochloride

just described; it is a colourless liquid, b. p. 204—206°, with an odour like carvone; the *semicarbazone*,  $C_9H_{14}N \cdot NH \cdot CO \cdot NH_2$ , crystallises in glistening leaflets, m. p. 149—150°.

[With WERNER LANGE.]—The oxidation of fencholic acid with potassium permanganate leads to the formation of (1) a *hydroxy-acid*,  $C_{10}H_{18}O_3$ , which crystallises in prisms, m. p. 80—81°; the corresponding *lactone*,  $C_{10}H_{16}O_2$ , has m. p. 11°, b. p. 134—135°/20 mm., 251—252°/760 mm.; (2) an isomeric *hydroxy-acid*,  $C_{10}H_{18}O_3$ , m. p. 110—112°, obtained only in very small quantities; (3) a *dihydroxy-acid*,  $C_{10}H_{18}O_4$ , compact crystals, m. p. 130—133°; the *lactone*,  $C_{10}H_{16}O_3$ , crystallises in prisms, m. p. 189—190°; (4) a *dihydroxy-acid*,  $C_{10}H_{18}O_4$ , m. p. 130°; the *lactone*,  $C_{10}H_{16}O_3$ , crystallises in needles, m. p. 70—71°.

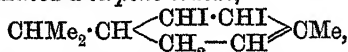
[With ALFRED HOMBERGER.]—*iso*Fenchone when treated with potassium hydroxide yields *isofencholic acid*,  $C_{10}H_{18}O_3$ , m. p. 33—34°; the *amide*,  $C_9H_{17} \cdot CO \cdot NH_2$ , has m. p. 65—66°; the *anilide* crystallises in needles, m. p. 100—101°.

II. *Behaviour of Monocyclic Ketones towards Potassium Hydroxide.*—The tendency of *cyclohexanone* and its homologues when heated with potassium hydroxide under pressure at 180—190° is to form condensation products rather than substances produced by fission of the ring.

[With MAX BEHNKE.]—*cyclo*Hexanone when heated with potassium hydroxide yields *cyclohexenyl-2-cyclohexanone* (compare Abstr., 1907, i, 220), dodecahydrotriphenylene (compare Mannich, Abstr., 1907, i, 205), a *substance*,  $C_{18}H_{26}O$ , crystallising in large prisms, m. p. 122—125°, an *acid*,  $C_{12}H_{20}O_2$ , b. p. 180—190°/19 mm., the *amide* of which,  $C_{12}H_{21}ON$ , crystallises in silvery leaflets, m. p. 96—97°, and an *acid*,  $C_{18}H_{28}O_2$ , b. p. 230—240°/19 mm.

2-Methyl*cyclo*hexanone yields an *acid*,  $C_{14}H_{24}O_2$ , b. p. 170—195°/18 mm.; the 3-methyl compound yields an *acid*,  $C_{14}H_{24}O_2$ , b. p. 185—195°/18 mm., and an *acid*,  $C_{21}H_{34}O_2$ , b. p. 230—240°/25 mm.; the 4-methyl compound yields an *acid*,  $C_{14}H_{24}O_2$ , b. p. 170—195°/18 mm., and an *acid*,  $C_{21}H_{34}O_2$ , b. p. 230—240°/20 mm. W. H. G.

**Additive Product of Iodine and Essential Oil of Turpentine.** CARLO CASANOVA (*Boll. chim. farm.*, 1909, 48, 684—685).—The action of iodine on turpentine oil proceeds energetically, and results in the formation of *p*-cymene:  $C_{10}H_{16} + I_2 = 2HI + C_8H_4MePr$ . If, however, the reaction takes place in presence of excess of the turpentine oil or with the addition of a diluent, such as almond oil, no hydrogen iodide is evolved, and by treating the mixture with alcohol, the author has separated a *terpene iodide*,

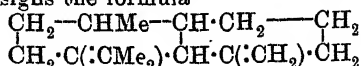


as a dense, yellowish-red, unstable liquid, b. p. 170°, at which temperature decomposition into hydrogen iodide, iodine, and *p*-cymene occurs; by the action of air or of light, the iodide decomposes with liberation of iodine.

T. H. P.

**Sesquiterpenes.** III. ERNST DEUSSEN (*Annalen*, 1909, 369, 41—62. Compare Deussen and Lewinsohn, Abstr., 1908, i, 353; Deussen, this vol., i, 171).—The author, from the results of his

investigations on the oxidation of  $\beta$ -caryophyllene and because it forms a blue nitrosite, assigns the formula



to this sesquiterpene.

[With A. LOESCHE and A. KLEMM.]—I. "*Caryophyllene*" from Oil of Clove-stalks.—It is proposed to name the nitrosate, m. p. 148—149°, described originally by Wallach and Tuttle,  $\alpha$ -caryophyllene nitrosate; the correct m. p. is 162°; when treated with benzylamine it yields  $\alpha$ -caryophyllenenitrolbenzylamine. The nitrosate, m. p. 131—132°, obtained by Deussen and Lewinsohn (Abstr., 1907, i, 945) from the blue caryophyllene nitrosite ( $\beta$ -caryophyllene nitrosite) is now designated  $d$ -caryophyllene nitrosate. The colourless isomeride, m. p. 139°, derived from  $\beta$ -caryophyllene nitrosite is named  $\beta$ -caryophyllene isonitrosite. The substance, m. p. 162—163°, obtained by the action of alcoholic potassium hydroxide on  $\beta$ -caryophyllene nitrosite cannot have the formula given previously (*loc. cit.*); it is either  $\text{C}_{15}\text{H}_{25}\text{O}_2\text{N}$  or  $\text{C}_{15}\text{H}_{28}\text{O}_2\text{N}$ .

The  $\alpha$ -compound obtained by Schreiner and Kremers (Abstr., 1900, i, 106) by the action of light on  $\beta$ -caryophyllene nitrosite is  $d$ -caryophyllene nitrosate, whilst the  $\beta$ -compound is identical with the substance,  $\text{C}_{15}\text{H}_{24}\text{O}_6\text{N}_4$ , m. p. 159°, formed by the action of hot light petroleum on the blue nitrosite.

A substance,  $\text{C}_{15}\text{H}_{28}\text{O}_2\text{N}$  or  $\text{C}_{15}\text{H}_{25}\text{O}_2\text{N}$ , has been isolated from the mother liquor obtained in the preparation of  $\alpha$ -caryophyllene nitrosochloride; it crystallises in slender needles, m. p. 125—125·5°,  $[\alpha]_D + 24^\circ$  (in benzene), and does not decolorise bromine.

$\alpha$ -Caryophyllene nitrosochloride when treated with sodium ethoxide or propoxide in alcoholic solution yields a *nitrosocaryophyllene*,  $\text{C}_{15}\text{H}_{23}\text{ON}$ , crystallising in rhombic plates, m. p. 128—129°, whilst with sodium methoxide it yields the optically inactive compound, m. p. 116° (*loc. cit.*), which is now shown to have the formula  $\text{C}_{15}\text{H}_{25}\text{ON}_2$ .

$\beta$ -Caryophyllene nitrosochloride, m. p. 159°, when heated with alcohol passes into the nitrosochloride, m. p. 122° ( $\alpha$ -isocaryophyllene nitrosochloride), derived from the sesquiterpene (*isocaryophyllene*) obtained during the preparation of  $\beta$ -caryophyllene nitrosite (*loc. cit.*); the nitrosochloride, m. p. 146° ( $\beta$ -isocaryophyllene nitrosochloride), when similarly treated also passes into the isomeride, m. p. 122°. The three nitrosochlorides when acted on by sodium methoxide yield a substance,  $\text{C}_{15}\text{H}_{25}\text{O}_2\text{N}$ , m. p. 162—164°, probably identical with that obtained in the preparation of  $\alpha$ -caryophyllene nitrosochloride (Abstr., 1907, i, 945).

A new *sesquiterpene*,  $\text{C}_{15}\text{H}_{24}$ , has been isolated from the "first runnings" obtained in the preparation of caryophyllene alcohol; it is a colourless oil, b. p. 126—127°/24 mm.,  $D_{19}^{20} 0.9227$ ,  $\alpha_D^{20} - 24^\circ$ ,  $n_D^{20} 1.49533$ .

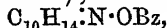
*iso*Caryophyllene when oxidised with potassium permanganate yields  $\alpha\alpha$ -dimethylsuccinic acid and the liquid ketonic or aldehydic acid, b. p. 196—198°/23 mm., described previously (Abstr., 1908, i, 171). The glycol formed by the oxidation of "caryophyllene" probably has the formula  $\text{C}_{14}\text{H}_{22}\text{O}_4$ , since it yields a crystalline *oxime*,  $\text{C}_{14}\text{H}_{23}\text{O}_4\text{N}$ , m. p. 187—188° (compare Haarmann, this vol., i, 400).

II. [With HANS PHILIPP.]—Gurjun balsam oil when oxidised with potassium permanganate in acetone yields a *ketone* or *aldehyde*,  $C_{15}H_{24}O$ , b. p. 170—180°/12 mm., which forms a crystalline *semicarbazone*,  $C_{15}H_{27}ON_3$ , m. p. 234° (decomp.).

III. [With A. KLEMM.]—A simple apparatus for use in the preparation of nitrosochlorides of mono- and sesqui-terpenes is described. The mixture of terpene, alcohol, ethyl acetate, and ethyl nitrite, contained in a tall glass vessel cooled by a freezing mixture, is stirred mechanically, and hydrochloric acid, likewise kept cold, is allowed to flow into the mixture drop by drop.

*Monoterpenes*. I. [With A. HAHN.]—*d*-Limonene nitrosochloride when treated with sodium methoxide yields a mixture of *l*-carvoxime ( $\alpha$ -carvoxime) and a new  $\beta$ -carvoxime, which may be separated through the benzoyl derivatives.

$\beta$ -Carvoxime,  $C_{10}H_{14}\cdot N\cdot OH$ , crystallises in glistening needles, m. p. 57—58°,  $[\alpha]_D + 68\cdot3^\circ$  (in benzene); the benzoyl derivative,



has m. p. 77°,  $[\alpha]_D + 75\cdot3^\circ$ .

II. [With HANS PHILIPP.]—Pinene nitrosochloride is converted by sodium methoxide into nitrosopinene and a *substance*,  $C_{11}H_{19}O_2N$ , probably formed by the replacement of chlorine by methoxyl; it has m. p. 101—102°.

W. H. G.

**Essential Oils.** HEINRICH HAENSEL (*Bericht von H. Haensel*, April–September, 1909. Compare this vol., i, 312).—A résumé of information on essential oils accumulated during the half-year April to September, 1909. The data recorded are mostly commercial, but the following are of scientific interest. The optical rotations quoted are for direct readings in a 100 mm. tube, except where otherwise stated.

Birch bud oil contains 73·2% of betulol, of which 29·6% occurs in the form of the acetate, and the rest free (compare von Soden and Elze, *Abstr.*, 1905, i, 451). *Ranunculus ficaria* herb in the flowering stage, free from roots, yielded 0·02% of a dark brown oil, which deposited solid matter on standing, and had a tobacco-like odour. The filtered oil,  $D^{24}_D$  0·9101, b. p. 150—310°, reduced ammoniacal silver solution. The solid deposit contained palmitic acid.

A sample of opoponax resin gave 3·46% of oil, having  $D^{19}_D$  0·8931, optical rotation in a 50 mm. tube  $-10\cdot3^\circ$ , soluble in 8·5 volumes of 95% alcohol.

The “terpenes,” separated in preparing “terpeneless orange oil” from oil distilled from unripe fruits, boiled at 171—175°, and contained *d*-limonene, but no camphene or pinene could be detected.

“Macassar” sandalwood yielded an oil having  $D^{19}_D$  0·9723,  $\alpha_D - 16\cdot92^\circ$ , saponification number 7·7, and acetyl ester number 206·6, corresponding with 96% of santalol. New Caledonian sandalwood furnished an oil having  $D^{20}_D$  0·9665,  $\alpha_D$  21·69° (direction not stated), saponification number 6·1, acetyl ester number 205·6, corresponding to 95·5% of santalol. Both these oils are soluble in two or more volumes of 70% alcohol.

Asparagus root oil gave 0·0108% of sour, strong-smelling, dark

brown oil, having  $D^{25}_D$  0.8777, saponification number 101, acid number 33, and yielding palmitic acid on saponification.

The roots of *Valeriana celtica* yielded 0.1% of thick yellow oil,  $D^{20}_D$  0.9693,  $n_D - 42^\circ$ , saponification number 62.5, acetyl ester number 71.9, which was miscible in all proportions with 90% alcohol, and boiled from 165—210°/45 mm. The portion boiling above 190° had  $D$  0.9359 and  $n_D - 30.88^\circ$ , and appeared to be a sesquiterpene. On saponification the oil yielded some palmitic acid.

The physical constants of "terpeneless oils," prepared from many well-known essential oils, are also quoted. T. A. H.

**Essential Oils.** SCHIMMEL & Co. (*Bericht*, October, 1909).—The "terpene portion" of ajowan seed oil contains *p*-cymene,  $\alpha$ -pinene, dipentene, and  $\gamma$ -terpinene.

*Artemisia herba-alba*, var. *densiflora* herb, yielded 0.58% of oil, having  $D^{15}_D$  0.8994,  $n_D + 14.05'$ ,  $n_D^{20}$  1.46684, acid number 4.6, ester number 35.0, and acetyl ester number 163.3. It is soluble in 1.8 parts of 70% alcohol, with the separation of some paraffin (compare this vol., i, 317).

Fiji "bay" oils had  $D^{15}_D$  0.9605—0.9893,  $n_D - 1^\circ$  to  $-2^\circ 10'$ , phenols 23—24%, and were soluble in 0.3 or more volumes of 90% alcohol. These oils were probably "light" bay oils only.

*Ocimum basilicum* oil, from Anjouan, had  $D^{15}_D$  0.9608,  $n_D + 0^\circ 40'$ , and  $n_D^{20}$  1.51425, and was soluble in five or more volumes of 80% alcohol (compare van Romburgh, *Abstr.*, 1901, i, 220; this vol., i, 597).

Birch bud oil, of this season's distillation, deposited crystals at  $+8^\circ$ , had  $D^{15}_D$  0.9730,  $n_D - 5^\circ 34'$ ,  $n_D^{20}$  1.50153, acid number 2.8, ester number 51.4, and acetyl ester number 150. The oil gave a clear solution with 0.25 volume of 90% alcohol, and deposited paraffin on further dilution.

A portion of camphor oil having b. p. 106—120°/7 mm.,  $D^{15}_D$  0.9378,  $n_D + 11^\circ$ ,  $n_D^{20}$  1.50188, contained bisabolene (Tucholka, *Abstr.*, 1897, ii, 584), but no cadinene.

*Chrysanthemum sinense*, var. *japonicum* flowers (?), yielded 0.8% of a yellowish-brown oil containing *i*-camphor and *l*-camphene (Keimatsu, *J. Ph. Soc. Japan*, 1909, 1).

African copaiba balsam oil gave results agreeing with those recorded by von Soden (this vol., i, 401), but whilst the original oil was strongly dextrorotatory, the cadinene isolated from the oil by way of the trihydrochloride proved to be levorotatory, and it is not certain whether the cadinene occurs in the oil in the *d*- or *l*-form.

Coriander oil, in which *d*-pinene and *d*-linalool had been recorded already, contained *d*- $\alpha$ -pinene, *i*- $\alpha$ -pinene,  $\beta$ -pinene, phellandrene (?), cymene, dipentene,  $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene (?), *n*-dec-aldehyde, geraniol, *l*-borneol, and acetic esters of the three alcohols.

Cumin fruit oil contained in the hydrocarbon portion, *d*- and *i*- $\alpha$ -pinenes,  $\beta$ -pinene, *p*-cymene (Wolpian's hydrocuminene was probably a mixture of these hydrocarbons),  $\beta$ -phellandrene, and dipentene. The aldehyde portion contained, in addition to cuminaldehyde, probably a *hydrocumininaldehyde*, since from the semicarbazones a portion melting at 200—201° was isolated and from the oximes a fraction having

m. p. 72—76°. The alcohol portion consisted of cumin alcohol and a small quantity of an unidentified alcohol.

The hydrocarbon portion of lemon oil consists mainly of *d*-limonene with a considerable quantity of *l*- $\beta$ -pinene, and small amounts of *l*- and *i*- $\alpha$ -pinenes, *l*-camphene,  $\beta$ -phellandrene, and  $\gamma$ -terpinene. No *p*-cymene could be detected. The sesquiterpene portion consists of cadinene(?) and bisabolene (Burgess and Page's "limene," *Trans.*, 1904, 85, 414; compare Tucholka, *Abstr.*, 1897, ii, 584).

Sweet orange oil, from Jamaica, had  $D^{15}$  0.8481 to 0.8488,  $\alpha_D^{20} + 97^\circ 47'$  to  $+ 98^\circ 2'$ , and bitter orange oil from the same locality had  $D^{15}$  0.8517 to 0.8521, and  $\alpha_D^{20} + 96^\circ 20'$  to  $+ 96^\circ 58'$ .

Eucalyptus oil, from the Transvaal, had  $D^{15}$  0.9236,  $\alpha_D + 1^\circ 45'$ ,  $n_D^{20}$  1.46337, contained 65% cineol, no phellandrene, and was soluble in 2.8 and more volumes of 70% alcohol.

It is suggested that Wallach and Grosse's sesquiterpene from pine needle oil (*Annalen*, 1909, 368, 19) may be bisabolene (see above).

Chamomile florets yielded 0.35% of viscous, deep blue oil, having  $D^{15}$  0.954,  $\alpha_D \pm 0$ ,  $n_D^{20}$  1.363734, and saponification number 74.4. The flower heads gave 0.51% of thick, greenish oil, having  $D^{15}$  0.949,  $\alpha_D \pm 0$ ,  $n_D^{20}$  1.363716, and saponification number 33.7.

*Lantana camara* oil, prepared in the Philippines, had  $D^{20}$  0.9132,  $\alpha_D^{30} + 11.5^\circ$ ,  $n_D^{30}$  1.4913 (Bacon, *Philippine J. Sci.*, 1909, 4, 127; compare this vol., i, 114).

French Lavender plants, grown during three years at Miltitz near Leipzig, yielded an oil having  $D^{15}$  0.8888,  $\alpha_D - 8^\circ 40'$ ,  $n_D^{20}$  1.46010, and contained 55.1% of linalyl acetate.

Lemon grass oil, from the Comores Islands, had  $D^{15}$  0.8914, and contained 83% citral. Samples from Jalpaiguri, in North Bengal, had  $D^{15}$  0.8924 to 0.8954,  $\alpha_D - 0^\circ 28'$  to  $- 0^\circ 49'$ , and citral 87 to 90% (acid sulphite process). All three were of the "insoluble" type.

The following limiting values for "hand-pressed lime oil" are suggested:  $D^{15}$  0.878 to 0.901,  $\alpha_D + 32^\circ 50'$  to  $+ 37^\circ 50'$ ,  $n_D^{20}$  1.482 to 1.486, acid number 3, ester number 18 to 30, non-volatile residue 10 to 14%, cloudy solution in 4 to 10 volumes of 90% alcohol.

Rosaceous fruit kernels gave the following yields of volatile oil: cherry, 0.7%; apricot, 1.6%; plum, 0.3 to 0.46%; bitter almonds, 0.81%; the aldehyde content of these varied from 61.8 to 88.7%.

*Piper camphoriferum* leaves gave 1.11% oil, having  $D^{20}$  0.9500 and  $\alpha_D + 19^\circ 21'$ , and contained camphor, borneol, terpenes, and a sesquiterpene. *Piper lineatum* leaves furnished 0.44% oil, b. p. 140—160°/15 mm.,  $D$  0.958, and  $\alpha_D + 8^\circ 45'$ . Camphor and phenyl ethers were absent. *Piper angustifolium*, var. *ossanum*, leaves furnished 0.87% oil containing camphor and borneol. "Matico" leaves, consisting mainly of *Piper acutifolium*, var. *subverbascifolium*, mixed with a few leaves of *P. asperifolium* and *P. mollicornum*, gave 0.8% oil, having  $D^{20}$  1.10,  $\alpha_D + 24'$ , methoxyl 21.8 to 22.1%. It contained pinene, sesquiterpene, dillisoapiol, and dillapiol (compare this vol., i, 316).

Rabak observed that leaves of *Mentha arvensis*, var. *glabrata*, grown in S. Dakota, gave 0.8% oil, having  $D$  0.9267,  $\alpha_D + 16^\circ 27'$ , acid number 2.6, ester number 13.1.

*Schinus molle* leaves, from Algeria, Grasse and Mexico, examined by

Roure-Bertrand fils, furnished an oil having  $D^{15}$  0.8492 to 0.8696,  $a_D + 42^\circ 30'$  to  $+ 65^\circ 20'$ ,  $n_D^{20}$  1.47616 to 1.47909, acid number 0.7 to 2.1, ester number 3.4 to 25.2, and acetyl ester number 29.4 to 56.5.

Celery oil, from herb and seed of wild celery, grown in S. France, was yellow, had a characteristic celery odour, and had  $D^{15}$  0.8713,  $a_D 58^\circ 30'$ ,  $n_D^{20}$  1.47715, acid number 1.8, ester number 41.5, and did not give a clear solution with 95% alcohol.

*Sium cicutaeifolium* herb, grown in S. Dakota, gave, according to Rabak, 0.5% oil, of yellow colour with an odour recalling those of caraway and turpentine oil. It had  $D^{22}$  0.8447,  $a_D + 63^\circ 40'$ , ester number 33, no free alcohols, gave a cloudy solution with 6 volumes of 90% alcohol, and probably contained *d*-limonene.

Juniper berry oil contained, in addition to pinene and cadinene already recorded, 4-terpinenol and a second alcohol, possessing an odour suggestive of borneol and geraniol, and having b. p. 105—110°/8 mm., 218—226°/760 mm.,  $D^{15}$  0.9476,  $a_D - 4^\circ 30'$ , and  $n_D^{20}$  1.48248. The phthalate boiled from 95—130° in the purest state obtained, so that a mixture of alcohols may be present. Other unidentified constituents of the oil occur in the fraction having b. p. 72—88°/8 mm.

*Curcuma zedoaria* roots gave 0.065% of a bluish-green oil, smelling of camphor and having  $D_4^{30}$  0.933,  $n_D^{30}$  1.4920,  $a_D^{30} < + 1.5^\circ$ . A quantity of a volatile crystalline substance was also obtained.

Lebanon cedar (*Cedrus Libani*) wood gave 3.5% of lemon-yellow oil of balsamic odour, and reminiscent of methyl heptenone and thujone. It had  $D^{15}$  0.9427,  $[\alpha]_D + 80^\circ 20'$ ,  $n_D^{20}$  1.51254, acid number 0.5, ester number 3.0, acetyl ester number 19.8, and dissolved in five to six volumes of 95% alcohol.

Bolivian copaiba balsam, from *Copaiba paupera*, had  $D^{15}$  0.998,  $a_D^{15} + 36^\circ$ ,  $n_D^{20}$  1.522, acid number (indirect) 89.7, saponification number (cold) 97.25. On distillation it furnished 23% oil, having  $D^{15}$  0.916,  $a_D + 18^\circ$ ,  $n_D^{20}$  1.5048, and of which 70% distilled from 250—270°, and probably contained cadinene and caryophyllene (Hartwich, *Schweiz. Woch. Chem. Pharm.*, 1909, 47, 373).

Tahiti vanilla yielded, according to Walbaum, besides vanillin, an oil heavier than water and boiling at 105—118°/6 mm., and containing anisaldehyde, anisic alcohol, and anisic acid.

A résumé of recent work on the constituents of essential oils, new analytical processes, and a bibliography of recent works relating to the chemistry, botany, and pharmacology of the subject are also given.

T. A. H.

**Turpentine of Aleppo Pine.** MAURICE VÈZES (*Bull. Soc. chim.*, 1909, [iv], 5, 931—933).—Three samples of turpentine from the Aleppo pine (*Pinus halepensis*), collected in France and in the Province of Oran in Algeria, have furnished the following percentage results on analysis. Turpentine oil 14.7—27.0, dry residue (rosin) 66.7—78.3, solid impurities 0.8—6.6, water and loss 2.1—5.5 (compare Tschirch and Schulz, *Abstr.*, 1907, i, 544). The turpentine oils obtained by the steam distillation of five samples of the oleo-resin had  $D^{20}$  0.8552—0.8568,  $[\alpha]_D + 46.6^\circ$  to  $+ 47.6^\circ$  and  $n_D^{20}$  1.4638—1.4652. On redistillation, 80% of each of the oils passed over at 155—156°, and

these fractions had  $D_{25}^{25}$  0.8541—0.8547,  $[\alpha]_D + 47.4^\circ$  to  $+48.4^\circ$ , and  $n_D^{25}$  1.4633—1.4639 (compare Tsakalotos, *Archimedes*, 1908, No. 1). It is concluded that at least 80% of the oil consists of *d*-pinene.

T. A. H.

**Chemical Examination of Jalap.** FREDERICK B. POWER and HAROLD ROGERSON (*Pharm. J.*, 1909, [iv], 29, 7—8).—Jalap consists of the dried tuberous roots of *Exogonium purga*, and on extraction with alcohol yields a product which, after washing with water, constitutes the "jalap resin" of medicine. This has been generally assumed by investigators to consist of two amorphous glucosidic constituents, one soluble in ether, the other insoluble, the latter being called "convolvulin." Numerous divergent formulæ have been assigned to convolvulin (compare Taverne, *Abstr.*, 1895, i, 119; Kromer, *Abstr.*, 1893, i, 423; 1894, i, 540, and 1896, i, 385; Höhnelt, *Abstr.*, 1897, i, 228). The present investigation shows that jalap resin is much more complex than has been supposed previously, that its physiologically active components are all indefinite and amorphous, as are also the most important products of their hydrolysis, and that consequently there is no justification for assigning empirical formulæ to these substances.

The jalap used was exhausted with hot alcohol, and from the extract so prepared the following products were obtained by (a) steam distillation, (b) extraction with water, and (c) successive extraction with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

A small quantity of volatile oil, b. p. 80—160°/60 mm.,  $D_{20}^{20}$  0.8868,  $[\alpha]_D$  0, possessing a smoky, disagreeable odour, and a yellow colour which gradually darkened.

The aqueous extract contained colouring matter and a sugar which yielded *d*-phenylglucosazone.

The residue ("jalap resin") yielded 1.9% to light petroleum. This dissolved portion was physiologically inactive and contained free palmitic and stearic acids, and on hydrolysis yielded formic, butyric, and higher volatile acids, palmitic acid, and a mixture of unsaturated acids, including much linoleic acid. The unsaponifiable portion included a *phytosterol*,  $C_{27}H_{46}O$ , m. p. 134—135°,  $[\alpha]_D - 32.4^\circ$ , cetyl alcohol, and a *substance*,  $C_{18}H_{36}O$ , m. p. 56—57°, which gave the phytosterol reaction.

The ether extract amounted to 9.7% of the resin; it was purgative, and contained a small amount of *ipurganol*,  $C_{21}H_{32}O_2(OH)_2$ , m. p. 222—225°,  $[\alpha]_D - 44.9^\circ$ , which crystallised in colourless needles and gave the colour reactions of the phytosterols; its *diacetyl* derivative has m. p. 166—167° and  $[\alpha]_D - 36.0^\circ$ . The residue of the ether extract, after hydrolysis by alkalis, gave a little phytosterol, cetyl alcohol, volatile acids, and amorphous products.

The chloroform extract amounted to 24.1% of the resin, and was purgative. It yielded a little  $\beta$ -methylæsculetin, and, after hydrolysis, furnished formic, butyric, and *d*- $\alpha$ -methylbutyric acids and convolvulinic acid,  $C_{15}H_{30}O_3$ , and possibly a higher homologue of the latter. Some dextrose was also formed, so that a portion of the extract was glucosidic.

The ethyl acetate extract, which was also purgative, formed 22% of the resin, and, on hydrolysis with dilute alcoholic sulphuric acid, yielded products similar to those got from the ether extract.

The alcoholic extract amounted to 38.8% of the resin, and was purgative. It was an almost white powder, m. p. 150—160°,  $[\alpha]_D - 37.1^\circ$ . On fusion with potassium hydroxide, it yielded formic, acetic, butyric, valeric, and higher volatile acids, together with azelaic and sebacic acids. On hydrolysis with barium hydroxide, it furnished formic, butyric, and  $\alpha$ -methylbutyric acids, together with amorphous "hydrolysed resin"; the latter proved to be inactive physiologically, and was of complex composition, since it could be separated into various products by successive extraction with (I) ether, (II) chloroform, (III) ethyl acetate, and (IV) alcohol. These on hydrolysis with dilute sulphuric acid all yielded formic, butyric, and other acids and sugar. No. III gave also  $\alpha$ -methylbutyric acid, and No. IV furnished convolvulinolic acid and ipurolic acid; the latter has been obtained already from the stems of *Ipomoea purpurea* (Power and Rogerson, Abstr., 1908, ii, 725). No. IV also furnished sebacic acid on oxidation with nitric acid. Each of the four extracts of the hydrolysed resin appeared to be only partly glucosidic, and to contain a soluble organic acid which was unaffected by dilute sulphuric acid.

T. A. H.

**Preparation, Behaviour, and Quantitative Estimation of Pure Urobilin and of Urobilinogen.** D. CHARNAS (*Biochem. Zeitsch.*, 1909, 20, 401—430).—In the spectro-photometric investigation of urobilin, its extraordinary instability has hitherto not been sufficiently taken into account; the "acid" and "alkaline" modifications do not exist. Urobilin can only be prepared pure by exposing urobilinogen to light. The latter substance is prepared from urobilin by reduction with sodium amalgam, or, better, by alkaline fermentation of the urine, and is then purified. Pure urobilin has three times the absorptive power for light possessed by hydrobilirubin, so that the two substances cannot be identical. The spectro-photometric estimation of urobilin is carried out by means of Ehrlich's colour reaction with dimethylaminobenzaldehyde.

G. B.

**Uromelanin. The Decomposition Product of the Colouring Matter of Urine.** ST. DOMBROWSKI (*Zeitsch. physiol. Chem.*, 1909, 62, 358—366. Compare Gawinskiy, this vol., ii, 331).—Analyses have been made of the uromelanin obtained by boiling urochrome with hydrochloric acid. The black precipitate was washed with water, dried, and extracted with alcohol, carbon disulphide, and ether. The analyses agree with the formula  $C_{47}H_{44}O_{18}N_7S$ , and differ but little from the numbers given by Nencki's proteinochromogen. Since urochrome contains sulphur and uropyrrol does not, it is impossible that urochrome can be an anhydride of the latter.

J. J. S.

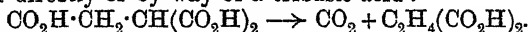
**Constitution of Aniline-black.** HANS T. BUCHERER (*Ber.*, 1909, 42, 2931—2933. Compare Willstätter and Dorogi, this vol., i, 535).—Willstätter and Dorogi have established that aniline-black can

be converted into benzoquinone with a yield of 95.44% of the theoretical, and in consequence of this, regard aniline-black as possessing an open-chain indamine structure. The author cites the great stability of emeraldine and aniline-black towards acids as opposed to this view, and considers the azine formula to be more probable in spite of the conversion of aniline-black into quinone. E. F. A.

**Action of Zinc Dust on Tannin.** LEO F. ILJIN (*J. pr. Chem.*, 1909, [ii], 80, 332—336).—When an approximately 10% aqueous solution of tannin is boiled with zinc dust for 15—20 hours, gallic acid is produced together with an amorphous substance,  $C_{56}H_{48}O_{34}$ , which resembles tannin in appearance, has  $[\alpha]_D^{25} + 24.1^\circ$  in 95% alcohol, gives coloured precipitates with many metallic salts, does not reduce Fehling's solution, and yields gallic acid when heated with 20% sulphuric acid in a current of hydrogen. C. S.

**Peculiarities in the Decomposition of Furan Derivatives.** HYPOLYT A. TREPHILIEFF and B. V. MANGUBI (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 875—885. Compare Abstr., 1907, i, 1063; 1908, i, 735).—The action of water on the tetrabromo-derivative of methronic acid results in the formation of succinic acid. The first phase of the action probably consists in the union of the furan ring with a molecule of water, and subsequent opening of the ring with formation of a  $\gamma$ -diketone:  $O < \begin{matrix} C(CHBr_2) \\ C(CBr_2 \cdot CO_2H) \end{matrix} = C \cdot CO_2H + H_2O =$   
 $CO_2H \cdot CBr_2 \cdot C(OH) : CH \cdot C(CO_2H) : C(OH) \cdot CHBr_2 \rightarrow$   
 $CO_2H \cdot CBr_2 \cdot CO \cdot CH_2 \cdot CH(CO_2H) \cdot CO \cdot CHBr_2$ .

Removal of the side groups from this compound then yields succinic acid, either directly or by way of a tribasic acid:



The action of bromine water on bromo-derivatives of furan containing a methyl group in the 3-position yields a tetrabromopropane and methylsuccinic acid, whilst when the methyl group is in the 2-position, as in methronic acid, only oxalic acid is obtained.

The action of bromine water on 3-carboxy-2-methylfuran-4-acetic acid (compare Feist, Abstr., 1899, i, 675) yields 5-bromo-4-methylfuran-2:3-dicarboxylic acid,  $O < \begin{matrix} CBr \\ C(CO_2H) \end{matrix} = CMe$   
 $: C \cdot CO_2H$ , m. p. 149—151°.

The interaction of methronic acid and bromine water in the cold yields two compounds in which the furan ring is probably not opened: (1) the compound,  $C_7H_2O_4Br_4$ , m. p. 129—130°, and (2) the compound,  $C_7H_2O_4Br_3$ , m. p. 138—139°. T. H. P.

**Methoxy-2-phenylcoumarones.** SIGMUND MOTYLEWSKI (*Ber.*, 1909, 42, 3148—3152).—The author extends to purely aromatic *o*-hydroxyketones the method of Kostanecki and Tambor (compare this vol., i, 319) for obtaining 2-substituted coumarones from *o*-hydroxyketones.

Benzoresorcinol monomethyl ether (2-hydroxy-4-methoxybenzophenone: compare Königs and Kostanecki, Abstr., 1907, i, 62) and

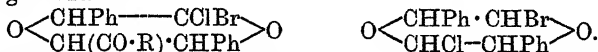
ethyl bromoacetate, when heated on the water-bath for twelve hours with an alcoholic solution of sodium, yield *ethyl 5-methoxy-2-benzoylphenoxyacetate*. After saponification with alcoholic potash, the unattacked ether is removed by means of carbon dioxide, and, on acidifying, the free acid is precipitated. The product is rendered impure by the presence of 5-methoxy-2-phenylcoumarilic acid, formed by intramolecular condensation from the 5-methoxy-2-benzoylphenoxyacetic acid primarily produced. The two are separated by fractional crystallisation from dilute alcohol, in which the latter acid is the more soluble. The *5-methoxy-2-benzoylphenoxyacetic acid* forms small, hexagonal laminæ, m. p. 114—115°. *5-Methoxy-2-phenylcoumarilic acid* forms rhombic laminæ or needles, m. p. 198° (decomp.). *5-Methoxy-2-phenylcoumarone* is formed by dry distillation of 5-methoxy-2-phenylcoumarilic acid, and also from 5-methoxy-2-benzoylphenoxyacetic acid by the action of acetic anhydride and sodium acetate. It forms colourless needles of m. p. 41—42°, and dissolves in concentrated sulphuric acid, giving a yellow colour. The products of the action of ethyl bromoacetate on hydrocotoin (benzophloroglucinol dimethyl ether or 2-hydroxy-4 : 6-dimethoxybenzophenone) are similar. *3 : 5-Dimethoxy-2-phenylcoumarilic acid* crystallises in colourless needles, m. p. 215°, with evolution of carbon dioxide. *3 : 5-Dimethoxy-2-benzoylphenoxyacetic acid* forms small, colourless laminæ, m. p. 140—141°. *3 : 5-Dimethoxy-2-phenylcoumarone* crystallises from alcohol in small, colourless laminæ or needles, m. p. 83—84°, and is slightly volatile in steam. Concentrated sulphuric acid dissolves it with production of a brownish-yellow colour. The fact that hydrocotoin enters into this reaction shows that it has the constitution above stated (compare Pollak, Abstr., 1898, i, 304).

The production of a corresponding coumarone from alizarin-yellow-A, which is obtained from benzoic acid and pyrogallol, shows that the substance is 2 : 3 : 4-trihydroxybenzophenone (compare E. Fischer, this vol., i, 309). On methylating benzopyrogallol (alizarin-yellow), a *mono-methyl ether* is obtained, which crystallises from alcohol in yellow laminæ, m. p. 164—165°. On further methylating this substance, *2-hydroxy-3 : 4-dimethoxybenzophenone* is produced as white laminæ, m. p. 120—121°. This yields directly by the above reaction, not the expected *5 : 6-dimethoxy-2-benzoylphenoxyacetic acid*, but *5 : 6-dimethoxy-2-phenylcoumarone*, which crystallises from alcohol in colourless laminæ, m. p. 83—84°, slightly volatile in steam. In concentrated sulphuric acid, it dissolves, giving a yellow coloration; on adding a trace of ferric chloride to the solution, the colour becomes green, and finally violet.

R. V. S.

**Constitution of the So-called Halogendiphenacyls.** OSKAR WIDMAN (*Ber.*, 1909, 42, 3261—3270).—Many objections are raised against the formulæ assigned by Paal and Schultze (compare Abstr., 1903, i, 707) to the  $\alpha$ - and  $\beta$ -halogendiphenacyls. It is shown that these compounds cannot contain hydroxyl or ketonic groups, or yet ethylene linkings, since they do not interact with acetic anhydride, phenylcarbimide, phenylhydrazine, hydrazine hydrate, hydroxylamine, bromine in chloroform, or potassium permanganate in glacial acetic acid.

The chemical properties of the  $\alpha$ - and  $\beta$ -isomerides (for example, the so-called  $\alpha$ - and  $\beta$ -bromodiphenaclys) are most clearly represented by the formula  $\begin{array}{c} \text{CHPh} \cdot \text{CBr} \cdot \text{O} \\ | \quad | \\ \text{O} \text{---} \text{CH} \text{---} \text{CHPh} \end{array}$ ; thus, when reduced by magnesium powder or sodium amalgam, they yield diphenacyl or diphenyltetramethylene glycol respectively, and when treated with acyl chlorides or bromides under pressure at  $100^\circ$ , or with hydrogen bromide or chloride in glacial acetic acid, yield additive products, which probably have the following formulæ:

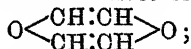


In agreement with the last formula, it is shown that the additive product of  $\beta$ -bromophenacyl with hydrogen chloride when acted on by sodium ethoxide in alcohol, yields a mixture of  $\alpha$ - and  $\beta$ -bromodiphenacyl, and when heated with red phosphorus and hydriodic acid yields acetophenone.

A substance having the constitution represented by the formula just assigned to the halogendiphenaclys must be capable of existing in a *cis*- and *trans*-form, in agreement with which is the fact that the chloro-, bromo-, and iodo-compounds are known in two isomeric forms which may be converted, either directly or indirectly, one into the other. It is not yet possible to state which isomeride has the *cis*- and which the *anti*-configuration.

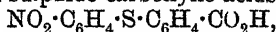
The  $\beta$ -iododiphenacyl described by Paal and Schultze (*loc. cit.*) is undoubtedly a mixture of the  $\alpha$ - and  $\delta$ -compounds, the latter being the true  $\beta$ -modification.

The  $\alpha$ - and  $\beta$ -halogendiphenaclys and their additive products are to be regarded, therefore, as derivatives of 1:4-dioxine,



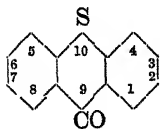
thus, the  $\alpha$ - and  $\beta$ -bromodiphenaclys are (*cis*-, *trans*-)-3-bromo-2:5-diphenyl-2:5-dihydrodioxines. W. H. G.

**Derivatives of Thiosalicylic Acid and of Thioxanthone.**  
FRITZ MAYER (*Ber.*, 1909, 42, 3046—3067. Compare this vol., i, 405).  
—Various nitrophenyl-sulphide-carboxylic acids,



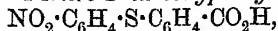
have been synthesised, but they do not yield nitrothioxanthenes when heated with sulphuric acid. The corresponding amino-compounds, however, readily lose water, yielding aminothioxanthenes. The nitrothioxanthenes can be prepared from the chlorides of the nitrophenyl-sulphide-carboxylic acids; they crystallise remarkably well, and their solutions in sulphuric acid have but a slight fluorescence. The aminothioxanthenes (numbering as in annexed formula), on the other hand, exhibit a strong green fluorescence. 2-Aminothioxanthone, which is analogous to  $\beta$ -aminoanthraquinone, does not yield an indanthrene derivative when fused with potassium hydroxide, or a flavanthrene derivative with antimony pentachloride in nitrobenzene solution.

When subjected to Skraup's synthesis, however, it yields a thioxanthoquinoline (compare Graebe, *Abstr.*, 1884, 759).

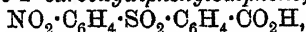


When oxidised with chromic acid, the nitrothioxanthenes yield the sulphones,  $C_6H_4 \begin{smallmatrix} SO_2 \\ \diagup \diagdown \\ CO \end{smallmatrix} C_6H_3 \cdot NO_2$ ; so far, the formation of sulphoxides has not been observed.

*p*-Nitrothioanisole has m. p. 71—72°, not 67° as stated by Blanksma (Abstr., 1902, i, 282). 4-Nitro-2'-carboxyphenyl sulphide,

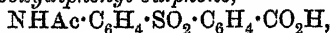


obtained by coupling a diazotised solution of anthranilic acid with a hot solution of sodium *p*-nitrophenylmercaptide, crystallises from alcohol in flat, yellow prisms, m. p. 229—231° after softening at 210°. The sodium salt forms deep red solutions; the methyl ester,  $C_{14}H_{11}O_4NS$ , has m. p. 131.5°; the ethyl ester,  $C_{15}H_{13}O_4NS$ , forms yellow needles, m. p. 127°. 4-Nitro-2'-carboxyphenylsulphoxide,  $NO_2 \cdot C_6H_4 \cdot SO \cdot C_6H_4 \cdot CO_2H$ , obtained by oxidising the sulphide with nitric acid or chromic acid, has m. p. 216—217°, and is identical with Weedon and Doughty's acid (Abstr., 1905, i, 345). The methyl ester,  $C_{14}H_{11}O_5NS$ , crystallises from acetic acid and light petroleum in slender needles, m. p. 143.5°, and the ethyl ester,  $C_{15}H_{13}O_5NS$ , has m. p. 107—107.5°. When the sulphide is oxidised with potassium permanganate, 4-nitro-2'-carboxydiphenylsulphone,



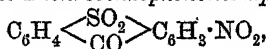
is formed. It crystallises from glacial acetic acid in compact, pale yellow cubes, m. p. 196.5°. The methyl ester has m. p. 136°, and the ethyl ester, m. p. 101°.

4-Amino-2'-carboxyphenyl sulphide,  $NH_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot CO_2H$ , obtained by reducing the nitro-compound with tin and alcoholic hydrogen chloride, crystallises from dilute alcohol in colourless plates, m. p. 193°. The hydrochloride forms colourless, felted needles, which decompose at 260°; the acetyl derivative,  $C_{15}H_{13}O_3NS$ , forms slender needles, m. p. 236—237°, and when oxidised with chromic acid yields 4-acetylamino-2'-carboxydiphenyl sulphone,



which has m. p. 215°.

2-Nitrothioxanthone,  $C_6H_4 \begin{smallmatrix} S \\ \diagup \diagdown \\ CO \end{smallmatrix} C_6H_3 \cdot NO_2$ , obtained by the action of phosphorus pentachloride on the sulphide, crystallises from glacial acetic acid in pale brown plates, m. p. 219—221°, and when oxidised with chromic acid yields 2-nitrobenzophenonesulphone,



which crystallises from acetic acid in flat plates, m. p. 254—255°.

2-Aminothioxanthone,  $C_{13}H_9ONS$ , obtained by reducing the nitro-compound, or by the action of sulphuric acid on the aminocarboxy-sulphide, crystallises from nitrobenzene in yellowish-brown plates, m. p. 221—222°. The hydrochloride,  $C_{13}H_9ONS \cdot HCl$ , decomposes at 230°. The acetyl derivative,  $C_{15}H_{11}O_2NS$ , crystallises in glistening plates, m. p. 236—237°. When 4-nitro-2'-carboxydiphenylsulphoxide is heated with phosphorus pentachloride or thionyl chloride, 2-nitrothioxanthone is formed, and not nitrobenzophenone sulphoxide.

Thioxanthone-1 : 2-(or 2 : 3)-quinoline,  $C_{16}H_9ONS$ , crystallises from

light petroleum in glistening, yellow needles, m. p. 167°. The *hydrochloride*,  $C_{16}H_9ONS \cdot HCl$ , crystallises from glacial acetic acid in needles, which decompose at 240—260°, and are hydrolysed by water.

*2-Nitro-2'-carboxyphenyl sulphide*,  $C_{13}H_9O_4NS$ , is prepared most readily by condensing methyl thiosalicylate with *o*-chloronitrobenzene, sodium methoxide, and a little copper powder at 140°, and hydrolysing the resulting ester. It crystallises from glacial acetic acid in yellow, nodular masses, m. p. 165—166°. The *methyl ester*,  $C_{14}H_{11}O_4NS$ , forms yellow crystals, m. p. 92°, and the *ethyl ester* has m. p. 75—76°. *2-Nitro-2'-carboxydiphenylsulphoxide*,  $C_{12}H_9O_5NS$ , obtained by oxidising an ester of the sulphide and subsequent hydrolysis, crystallises from glacial acetic acid in glistening, pale yellow plates, m. p. 277°. The *methyl ester*,  $C_{14}H_{11}O_5NS$ , has m. p. 147—148°, and the *ethyl ester*, m. p. 120°. The corresponding *sulphone*,  $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot C_6H_4 \cdot CO_2H$ , forms slender needles, m. p. 197—199°, and its *methyl ester*,  
 $C_{14}H_{11}O_6NS$ ,

has m. p. 127°.

*2-Amino-2'-carboxyphenyl sulphide*,  $NH_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot CO_2H$ , prepared by reducing the nitro-derivative with ammonia and ferrous sulphate, crystallises from glacial acetic acid in colourless nodules, m. p. 156—157·5°. The *acetyl derivative*,  $C_{15}H_{13}O_3NS$ , has m. p. 188—196°.

*4-Nitrothioxanthone* crystallises from benzene in yellow needles, m. p. 215°, and when oxidised with an excess of chromic acid yields *4-nitrobenzophenone sulphone*,  $C_{13}H_7O_5NS$ , which crystallises in brilliant, colourless needles, m. p. 240°. *4-Aminothioxanthone*,  $C_{13}H_9ONS$ , crystallises from benzene in glistening plates, m. p. 202—203°; the *acetyl derivative*,  $C_{15}H_{11}O_2NS$ , has m. p. 233—234°.

*3-Nitro-2'-carboxyphenyl sulphide*, prepared by condensing methyl thiosalicylate and *m*-iodonitrobenzene with sodium methoxide and copper powder at 160—170°, and hydrolysing the resulting ester, crystallises from glacial acetic acid, and has m. p. 168—169°. The *methyl ester* crystallises in yellow, rectangular plates, m. p. 112—114°, and when oxidised yields the *sulphoxide*,  $NO_2 \cdot C_6H_4 \cdot SO \cdot C_6H_4 \cdot CO_2Me$ , which crystallises from glacial acetic acid in colourless needles, m. p. 137—138°. The corresponding *acid*,  $C_{13}H_9O_5NS$ , has m. p. 222—223°, and the *carboxysulphone*,  $C_{13}H_9O_6NS$ , m. p. 190°. *3-Amino-2'-carboxyphenyl sulphide* crystallises from alcohol in pale yellow needles, m. p. 159—160°.

*1-Nitrothioxanthone* crystallises from benzene in pale yellow needles, m. p. 237°, and the corresponding *amino-compound* in greyish-brown needles, m. p. 249—250°. The *acetylamino-compound* has m. p. 273°.

*3-Nitro-6-carboxyphenyl sulphide*,  $CO_2H \cdot C_6H_3(NO_2) \cdot SPH$ , prepared by diazotising 4-nitro-2-aminobenzoic acid and coupling with an alkaline solution of phenyl mercaptan, crystallises in yellow nodules, m. p. 210—211°. The corresponding *amino-acid*,  $C_{13}H_{11}O_2NS$ , crystallises from methyl alcohol in compact cubes or glistening plates, m. p. 200—201°.

*3-Nitrothioxanthone* forms glistening prisms, m. p. 247°; the *3-amino-compound* has m. p. 246°, and its *acetyl derivative*, m. p. 267°.

o-Nitrophenyl mercaptan has m. p.  $56^{\circ}$ , not  $46^{\circ}$  as stated by Blanksma (*loc. cit.*), and its methyl ether, m. p.  $63-64^{\circ}$ . J. J. S.

**Sulphides from the Ester of 2:6-Dithiolketopenthiophen-3:5-dicarboxylate.** VI. HERMANN APITZSCH and C. KELBER (*Ber.*, 1909, 42, 2940—2943).—By the oxidation of ethyl 2:6-dithiol-4-ketopenthiophen-3:5-dicarboxylate, a termolecular sulphide is formed (this vol., i, 46, 47). By carrying out the oxidation with iodine quantitatively, it has been possible to establish the structure of this sulphide,  $C_{33}H_{30}O_{15}S_9$ , as  $\left( \begin{array}{c} CO_2Et \cdot C - CO - C \cdot CO_2Et \\ | \qquad \qquad | \\ -SC - S - CS- \end{array} \right)_3$ .

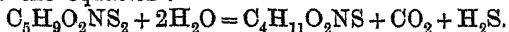
This termolecular sulphide is easily decomposed by alkalis into the original unimolecular mercaptan. A sulphinic acid is also formed, as shown by the formation of sulphurous acid when the alkaline solution is rendered acid.

When the dithiolketopenthiophendicarboxylate is oxidised with amyl nitrite, a disulphide,  $C_{22}H_{30}O_{10}S_4(SH)_2$ , is formed. This separates in radial bunches of thin, orange-red needles, m. p.  $158-159^{\circ}$ .

E. F. A.

**Cheiroline.** WILHELM SCHNEIDER (*Ber.*, 1909, 42, 3416—3420).—The numbers given by Wagner (Abstr., 1908, i, 202) and by the author (this vol., i, 118) for the proportion of sulphur in cheiroline are considerably lower than the true number, owing to the fact that a portion of the sulphur of this compound is combined in such a manner that its complete oxidation to sulphuric acid by means of fuming nitric acid in a sealed tube takes place only after protracted heating at a temperature not lower than  $300^{\circ}$ . The mean proportion of sulphur found in this way is 35.7%. Repetition of the estimation of carbon, hydrogen, and nitrogen by very slow combustion in a tube having double the ordinary length, and packed in the first half with copper oxide and in the second with lead chromate, gives numbers which correspond closely with the formula  $C_5H_9O_2NS_2$  (mol. wt. 179), which is also in agreement with the molecular weights in freezing ( $186-260$ ) and boiling benzene ( $220-271$ ).

This new formula for cheiroline affords a ready explanation of the resolution of this compound by means of dilute sodium hydroxide solution, which must be regarded as a simple hydrolysis taking place according to the equation:



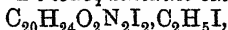
In wallflower seeds, cheiroline appears to exist in the form of a glucoside.

T. H. P.

**Iodine Derivatives of Cinchona Alkaloids.** TAD. KOZNIIEWSKI (*Bull. Acad. Sci. Cracow*, 1909, 734—746).—By adding a solution of iodine in carbon disulphide to a hot alcoholic solution of the alkaloids, *di-iodocinchonine*,  $C_{19}H_{22}ON_2I_2$ , orange-yellow crystals, m. p.  $147-149^{\circ}$ , and *di-iodoquinidine*,  $C_{20}H_{24}O_2N_2I_2$ , m. p.  $157-159^{\circ}$ , can be obtained; these substances are analogous to the strychnine and brucine derivatives previously described (Abstr., 1908, i, 1007). With

an excess of iodine, the much more soluble hydriodide is formed,  $C_{19}H_{22}ON_2I_2 \cdot HI, H_2O$  (= cinchonine periodide).

The di-iodo-derivatives yield with methyl iodide, *di-iodocinchonine methiodide*,  $C_{19}H_{22}ON_2I_2 \cdot CH_3I$ , m. p. 193—195°, and *di-iodoquinidine methiodide*,  $C_{20}H_{24}O_3N_2I_2 \cdot CH_3I$ , m. p. 194—197°, which can also be obtained by adding an iodine solution to cinchonine and quinidine methiodide respectively. *Di-iodoquinidine ethiodide*,



has also been prepared.

G. B.

**Formation of *i*-Nicotine from Methyl- $\delta$ -3-pyridylbutylamine (Dihydrometanicotine).** KARL LÖFFLER and SAMY KOBER (*Ber.*, 1909, 42, 3431—3438).—The reaction for the preparation of 1-alkylpyrrolidines (this vol., i, 830) has been applied to the production of *i*-nicotine from dihydrometanicotine. Metanicotine, obtained from nicotine by Pinner's method (*Abstr.*, 1894, i, 388), is heated with fuming hydriodic acid and amorphous phosphorus at 100° for fifteen hours, and the resulting iodo-compound is treated for twenty-four hours with zinc dust in a freezing mixture, 25% hydrochloric acid being added subsequently, and, after one day, the mixture is heated on the water-bath. The *dihydrometanicotine*,  $C_8NH_4 \cdot C_4H_9 \cdot NHMe$ , is then liberated by sodium hydroxide and purified through the *picrate*, m. p. 161—162°. The base itself has b. p. 258—259° and  $D_4^{25}$  0.959, and forms an *aurichloride*, m. p. 138°, and a *platinichloride*, m. p. 198—199° (decomp.). By treatment with sodium hypobromite, it yields the *N*-brominated derivative, an unstable, yellow oil, which is converted into nicotine by concentrated sulphuric acid under definite conditions.

C. S.

**$\psi$ -Codeine.** LUDWIG KNORR, HOWARD BUTLER, and HEINRICH HÖRLEIN (*Annalen*, 1909, 368, 305—323. Compare *Abstr.*, 1907, i, 151, 789, 956; 1908, i, 41, 42, 361).—A further contribution to the chemistry of  $\psi$ -codeine.

*Benzoyl- $\psi$ -codeine hydrochloride*,  $C_{25}H_{25}O_4N, HCl$ , crystallises in small, white needles, m. p. 174—184°; the *methiodide*,  $C_{25}H_{25}O_4N, MeI$ , forms small, silky needles, m. p. 206—208° (decomp.).  $\psi$ -Codeine yields with phenylcarbimide the *anilino-carboxylic ester*, the *hydrochloride* of which,  $C_{25}H_{26}O_4N_2, HCl, Et \cdot OH$ , crystallises in stellate aggregates of prisms, m. p. 73—94° (decomp.), whilst the *methiodide*,



has m. p. 243—244°. *Chloro- $\psi$ -codeine*,  $C_{18}H_{20}O_3NCl$ , prepared by the addition of potassium chlorate to a solution of the base in dilute hydrochloric acid, forms glistening, white needles, m. p. 203—204°,  $[\alpha]_D^{25}$  -100.8° (in 99% alcohol). *Bromo- $\psi$ -codeine*,  $C_{18}H_{20}O_3NBr$ , crystallises with 1Et·OH in small, silky, white needles, m. p. 190—192°,  $[\alpha]_D^{25}$  -75.2° (in 99% alcohol). *Nitro- $\psi$ -codeine*,  $C_{18}H_{20}O_3N_2$ , crystallises in rectangular leaflets, m. p. about 235° (decomp.),  $[\alpha]_D^{25}$  -49.9° (in chloroform).

The action of phosphorus pentachloride on  $\psi$ -codeine leads to the formation of a mixture of  $\alpha$ -chlorocodide and  $\psi$ -chlorocodide; the *methiodide* of the latter,  $C_{18}H_{20}O_3NCl, MeI$ , crystallises in glistening leaflets and cubes, m. p. 185—186° (decomp.),  $[\alpha]_D^{25}$  -227.4° (0.102 gram in 20 c.c. of alcohol + water, 1:3), -229° (0.197 gram in 20 c.c.

of the same solvent).  $\psi$ -Codeine when treated with phosphorus tribromide yields bromocodeine (compare Schryver and Lees, *Trans.*, 1901, 79, 575).

$\epsilon$ -Methylmorphimethine (compare *Abstr.*, 1907, i, 151) crystallises in tetragonal pyramids, m. p. 129—130°,  $[\alpha]_D^{25} - 120.1^\circ$  (in 99% alcohol); the hydrochloride has  $[\alpha]_D^{25} - 154^\circ$  (in water); the methiodide has  $[\alpha]_D^{25} - 111^\circ$  (in water); acetyl- $\epsilon$ -methylmorphimethine methiodide has  $[\alpha]_D^{25} - 45^\circ$  (in water). Attempts to obtain a sixth methylmorphimethine by treating the  $\epsilon$ -isomeride with aqueous and alcoholic potassium hydroxide were unsuccessful.  $\epsilon$ -Methylmorphimethine is decomposed by acetic anhydride at 180°, yielding acetylmethylmorphol and ethanoldimethylamine, whilst the methiodide when treated with alcoholic potassium hydroxide at 160°, yields morphenol and trimethylamine (compare Vongerichten, *Abstr.*, 1901, i, 742). W. H. G.

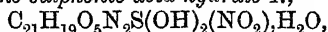
**Strychnine Alkaloids. VI. Preparation of Brucinesulphonic Acids and Cause of the Nitric Acid Reaction for Brucine.** HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1909, 42, 3067—3075).—Brucine, when treated in the same manner as strychnine (this vol., i, 671), gives rise to three isomeric sulphonic acids. It is considered that the base contains the grouping  $R'CHR'''CH_2R''$ , and that the three acids are formed by the replacement of the three hydrogen atoms; two of the acids are therefore stereoisomeric. The sulphonic acids are feeble acids, their alkali salts being decomposed by carbon dioxide, and the basic character of the alkaloid is so completely destroyed that the compounds do not form salts with acids.

The product obtained by the action of manganese dioxide and sulphurous acid at 70—80°, and subsequent cooling with ice, is a mixture of sulphonic acids I. and II.; the filtrate from these, when kept for several weeks, yielded the acid III. The acids I. and II. can be separated by fractional solution in, and crystallisation from, hot water.

*Brucinesulphonic acid* I.,  $C_{23}H_{26}O_7N_2S$ , crystallises from hot water, in which it is moderately soluble (1:12), in long, colourless crystals, which change colour at 280°, but are not molten at 300°. Its solution in sodium hydroxide has  $[\alpha]_D^{20} - 242^\circ$ . The *sulphonic acid* II. is less soluble in hot water (1:55), and crystallises in flat, rectangular plates; it turns brown at 200°, and has m. p. 260° (decomp.) and  $[\alpha]_D^{20} + 29^\circ$  in sodium hydroxide solution. The *sulphonic acid* III. crystallises from hot water in pointed, broad prisms; it turns brown at 180°, and has m. p. 245° (decomp.) and  $[\alpha]_D^{20} + 156.8^\circ$ . It has the same solubility as acid II. in water.

The sulphonic acid I. reacts readily with dilute nitric acid, yielding short, bright red prisms of the *quinone*,  $C_{21}H_{20}O_7N_2S \cdot 3H_2O$ , which is only sparingly soluble in the usual organic solvents, but which dissolves readily in alkalis. When reduced with sulphurous acid, it yields the *quinol*,  $C_{21}H_{22}O_7N_2S \cdot 3H_2O$ , which crystallises from water in colourless needles. The quinone is undoubtedly formed from brucinesulphonic acid by the elimination of methyl from two  $O \cdot CH_3$  groups and the oxidation to an orthoquinone,  $OC \begin{array}{c} \diagup CO \cdot CR' \\ \diagdown CR'' \cdot CR''' \end{array} N \cdot COR$ .

A by-product formed during the preparation of the quinone is *didemethylnitrobrucine sulphonic acid hydrate* I.,

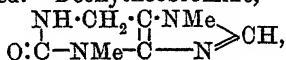


which crystallises from hot water in glistening, yellow needles. This compound is analogous to Moufang and Tafel's cacothelin (Abstr., 1899, i, 309).

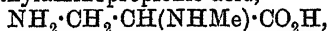
The unstable red compound obtained by the action of nitric acid on brucine is undoubtedly a quinone analogous to the quinonesulphonic acid described above.

J. J. S.

**Diamino-acids from Deoxyxanthines.** JULIUS TAFEL and EDWARD P. FRANKLAND (*Ber.*, 1909, 42, 3138—3146).—In their investigation on deoxycaffeine, Baillie and Tafel observed the production of barium carbonate and barium formate when the substance was boiled with barium hydroxide (Abstr., 1900, i, 121). Continuing the examination of this hydrolysis in the case of deoxycaffeine and of deoxytheobromine, the authors have now isolated the diamino-acids which are also produced. Deoxytheobromine,



yields  $\beta$ -amino- $\alpha$ -methylaminopropionic acid,



whilst from deoxycaffeine,  $\alpha\beta$ -dimethylaminopropionic acid,  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{NHMe})\cdot\text{CO}_2\text{H}$ , is obtained. The new acids resemble diaminopropionic acid, especially in the power of forming, with one equivalent of an acid, salts which are stable towards water and insoluble in alcohol.

**Hydrolysis of Deoxytheobromine with Baryta.**—The method of preparation previously given for deoxytheobromine may be simplified by directly neutralising with ammonia after the reduction. Yield 90%. The hydrolysis is effected by boiling with 10 parts of barium hydroxide in 50 parts of water for five hours.  $\beta$ -Amino- $\alpha$ -methylaminopropionic acid crystallises in well-developed prisms, m. p., on rapid heating, towards  $160^\circ$  (decomp.). The monohydrochloride forms flat, rhombic plates; it turns brown above  $200^\circ$ , m. p.  $210\text{--}212^\circ$  (decomp.). The dihydrochloride, prepared by treating the acid with concentrated hydrochloric acid, forms crystals resembling saltpetre, m. p.  $190\text{--}192^\circ$  (decomp.). When warmed with water, it yields the monohydrochloride. The sulphate,  $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2\cdot\text{H}_2\text{SO}_4$ , crystallises in well-formed tetrahedra, which soften at  $165^\circ$ , m. p.  $185\text{--}188^\circ$  (decomp.). The nitrate,  $\text{C}_4\text{H}_{10}\text{O}_2\text{N}_2\cdot\text{HNO}_3$ , crystallises from water in prisms, m. p. about  $185^\circ$  (decomp.). The ethyl ester hydrochloride is prepared by boiling the hydrochloride of the acid with alcoholic hydrochloric acid for eighteen hours. The acid itself is only very slowly attacked under these conditions. Crystalline solid, m. p. about  $176^\circ$  (decomp.). The dibenzoyl derivative is an imperfectly crystalline powder, m. p.  $202\text{--}204^\circ$ .  $\beta$ -Amino- $\alpha$ -methylnitrosoaminopropionic acid is prepared by acting on the monohydrochloride of the acid with silver nitrite; it crystallises in small tetrahedra, which are anhydrous; it decomposes at  $210\text{--}212^\circ$ . The nitrosoamine gives Liebermann's reaction very

distinctly. On heating with dilute hydrochloric acid, the above-described dihydrochloride of  $\alpha$ -methylamino- $\beta$ -aminopropionic acid is produced.

*Hydrolysis of Deoxycaffeine with Baryta.*—The hydrolysis is best effected at a lower temperature ( $80^\circ$ ), and requires longer heating (fifty hours) than that of deoxytheobromine. Free  $\alpha\beta$ -dimethylamino-propionic acid shows much less inclination to crystallise than the monomethylated acid. The monohydrochloride crystallises from water and methyl alcohol in stellar aggregates of prisms, and has m. p. about  $180^\circ$  (decomp.). It was not found possible to prepare from it a dihydrochloride. The ethyl ester hydrochloride is prepared by warming a concentrated aqueous solution of the monohydrochloride with alcoholic hydrochloric acid for a few minutes; on cooling, the substance separates out as a granular, crystalline precipitate. When heated it melts partly at  $120$ – $125^\circ$ , solidifies again, and finally decomposes towards  $180^\circ$ . Mononitrosoamines of  $\alpha\beta$ -dimethylaminopropionic acid were obtained by the action of silver nitrite as above. One crystallised in rectangular plates (from water) and had m. p.  $270^\circ$  (decomp.), and showed Liebermann's reaction. The other crystallised from water in needles, m. p.  $186^\circ$ . These are probably the two isomerides which would be expected. The dinitrosoamine was obtained as an acid syrup, which showed Liebermann's reaction.

R. V. S.

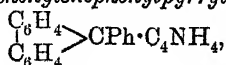
**New Preparation of 1-Alkylpyrrolidines.** KARL LÖFFLER and CURT FREYTAG (*Ber.*, 1909, 42, 3427–3431).—A method which seems to be general for the preparation of 1-alkylpyrrolidines from aliphatic amines of the type of methylbutylamine or methylisocamylamine is the following. Methylbutylamine is shaken with a strongly cooled solution of sodium hypobromite. The resulting *N*-bromomethylbutylamine is added slowly to concentrated sulphuric acid, and the mixture is heated, at first for three hours on the water-bath and finally at  $135^\circ$  for thirty minutes. The base, liberated by sodium hydroxide and purified through the picrate, m. p.  $221^\circ$ , is proved to be 1-methylpyrrolidine.

C. S.

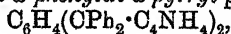
**Condensation of Aromatic Carbinols with Pyrrole.** EUGEN KHOTINSKY and RAPHAEL PATZEWITCH (*Ber.*, 1909, 42, 3104–3106).—Tertiary carbinols of the type of triphenylcarbinol condense with pyrrole in the presence of acetic acid. Anthranol and primary and secondary alcohols do not condense with pyrrole.

*Triphenylpyrrylmethane*,  $\text{C}_6\text{H}_5 \cdot \text{C}_4\text{NH}_4$ , obtained by boiling a glacial acetic acid solution of triphenylcarbinol and pyrrole, is sparingly soluble in most solvents, but crystallises from ethylene bromide or nitrobenzene and has m. p.  $253^\circ$ . *Diphenyl-p-anisylpyrrylmethane*,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_5 \cdot \text{C}_4\text{NH}_4$ ,  
has m. p.  $172$ – $176^\circ$ ; *diphenylenephenylpyrrylmethane*,



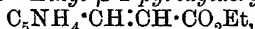
has m. p.  $210^\circ$ , and *tetra- $\omega$ -phenyldi- $\omega$ -pyrryl-p-xylene*,



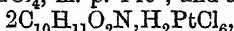
obtained from tetraphenylxylene glycol and pyrrole, has no definite m. p. All condensation products give the pine wood reaction.

J. J. S.

**2-γ-Hydroxypropylpiperidine and a New Synthesis of Piperolidine (δ-Coniceine).** KARL LÖFFLER and MAX FLÜGEL (*Ber.*, 1909, 42, 3420—3427).—*Ethyl β-2-pyridylacrylate*,



b. p. 161°/25 mm., is obtained by the action of hydrogen chloride on a hot alcoholic solution of the hydrochloride of pyridylacrylic acid and subsequent treatment by potassium carbonate. It forms an *aurichloride*,  $C_{10}H_{11}O_2N \cdot HAuCl_4$ , m. p. 149°, and a *platinichloride*,



m. p. 114°. It is reduced by sodium and hot ethyl alcohol to 2-γ-hydroxypropylpiperidine,  $C_8NH_{10} \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$ , b. p. 248°,  $D_4^{15}$  1.0043, which is best purified as the *hydrochloride*,  $C_8H_{17}ON \cdot HCl$ , m. p. 128°. The *mercurichloride*,  $C_8H_{17}ON \cdot HCl \cdot 6HgCl_2$ , has m. p. 182—183°. Piperolidine is obtained when 2-γ-hydroxypropylpiperidine is heated for six hours with fuming hydriodic acid and amorphous phosphorus in a sealed tube at 125°, and the isolated product is heated on the water-bath with an alkali for thirty minutes.

When 2-γ-hydroxypropylpiperidine is heated with phosphoric oxide at 135° for three hours, or with glacial acetic and concentrated sulphuric acids at 160—165° for three to four hours, a mixture of piperolidine and 2-*allylpiperidine*, containing chiefly the former, is obtained, which is separated by means of the picrates. The production of piperolidine in these two reactions illustrates the greater ease of formation of five- than of four-membered rings, since 2-β-hydroxypropylpiperidine does not yield 2-methylconidine under these conditions. Moreover, the 2-*allylpiperidine*,  $C_8NH_{10} \cdot CH_2 \cdot CH:CH_2$ , b. p. 170—171°,  $D_4^{15}$  0.8823 (*hydrochloride*, m. p. 202—203°; *aurichloride*, m. p. 101°; *platinichloride*, m. p. 174°), is not identical with either of the unsaturated bases obtained by dehydrating 2-β-hydroxypropylpiperidine (this vol., i, 180), thus furnishing another proof that these two bases are stereoisomerides and not structurally different (this vol., i, 324).

C. S.

**A New Instance of Nitrogen Isomerism in the Piperidine Series.** ALBERT LADENBURG and W. SOBECKI (*Ber.*, 1909, 42, 3152—3156).—The indications of the existence of isomeric forms which were met with in the case of coniine (*Abstr.*, 1906, i, 692; 1907, i, 956) and of stilbazoline (*Abstr.*, 1904, i, 92, 1048) have now again shown themselves in the case of benzyl-α-pipecoline. Active *d*-benzyl-pipecoline has a different rotatory power according to the mode of preparation employed. Pure *r*-pipecoline and benzyl chloride react with development of heat, forming *r*-benzylpipecoline, which has b. p. 160—162°/47 mm. or 267° (corr.) at atmospheric pressure. The resolution of the base was effected by means of the hydrogen tartrate. After nine recrystallisations of the hydrogen tartrate, the liberated base had  $\alpha_D^{25} +48.5^\circ$  when examined in a tube 49.65 mm. long. Optically active *d*-pipecoline was also benzylated in the same way, and

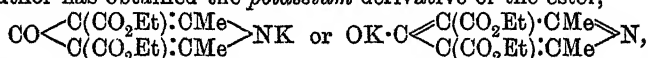
the active benzylpipercoline purified first by fractionation and then by recrystallisation of the hydrogen tartrate. After four recrystallisations, the liberated base had  $\alpha_D^{25} + 50.1^\circ$  when examined in the above tube. The difference in rotatory power was not accompanied by any marked differences in other respects.

*d*-Benzylpipercoline from *r*-pipercoline has  $D^{21}_D$  0.9527 and  $n_D$  1.5187. The hydrogen tartrate has m. p. 67—69°. The aurichloride has m. p. 110—112°.

*d*-Benzylpipercoline from *d*-pipercoline has  $D^{21}_D$  0.9525 and  $n_D$  1.5182. The hydrogen tartrate has m. p. 67—69°, and the aurichloride has m. p. 112—114°. R. V. S.

**The Relationship of Pyridine to the Sugars.** CARL NEUBERG (*Biochem. Zeitsch.*, 1909, 20, 526—530).—Attention is called to the frequent conversion, especially in plants, of sugars into cyclic substances, and of cyclic substances into sugars. Pyridine can be converted into a carbohydrate-like substance from which furfuraldehyde can be obtained by distillation with sulphuric acid, from which distillate it was isolated in the form of its *p*-nitrophenylhydrazine derivative. The conversion of the pyridine into the carbohydrate-like substance was brought about by hydrogen peroxide in the presence of sulphuric acid and ferrous sulphate. The yield was very small. S. B. S.

**Characteristics of Ethyl Lutidonedicarboxylate.** TH. SABANIEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 789—791).—By dissolving ethyl lutidonedicarboxylate in dilute potassium hydroxide solution and precipitating with excess of concentrated potassium hydroxide solution, the author has obtained the *potassium* derivative of the ester,



which is not methylated by the ordinary methods, and gives an almost quantitative yield of lutidonedicarboxylic acid when heated with ethyl iodide and ethyl alcohol in a sealed tube at 150°. This hydrolysing action of a mixture of ethyl iodide and ethyl alcohol is also shown with ethyl diphenylpyridonedicarboxylate, which is converted into the corresponding acid. Under similar conditions, ethyl dimethylpyrone-dicarboxylate gives a good yield of dimethylpyrone. T. H. P.

**Constitution of Anthranil.** VI. GUSTAV HELLER (*J. pr. Chem.*, 1909, [ii], 80, 320—331).—In connexion with the non-production of anthranil from anthroxanic acid (*Abstr.*, 1908, i, 267), Bamberger's criticism (this vol., i, 509) and comparison of anthroxanic acid with isooxazolecarboxylic acids are not justifiable, since the stabilities of monocyclic and dicyclic molecules are not strictly comparable. Bamberger and Elger's experiment, the heating of anthroxanic acid and water at 150°, has been repeated, with utterly different results. The product is not anthranil, as they claim, but aniline. Its production is explained by the elimination of carbon dioxide from the anthroxanic acid with the formation of anthroxan, which absorbs water, yielding anthranilic acid, from which the aniline is produced by loss of

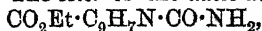
carbon dioxide. Anthranil and water at 153—156° do not yield aniline (this fact is additional evidence of the different constitutions of anthranil and anthroxan), but a yellow, crystalline condensation product, m. p. 245°.

Bamberger and Lublin's experiment with methylantranil (methyl-anthroxan), 23% hydrochloric acid, and sodium nitrite (*loc. cit.*) has been repeated; methylantranil dichloride (methylanthroxan dichloride) and a diazo-salt are produced, but not *o*-acetylphenylnitrosohydroxylamine. The paper concludes with a short discussion of the constitution of anthranil and the possibility of tautomerism. C. S.

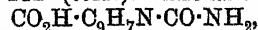
**1-Methylindole-2:3-dicarboxylic Acid and 2-Amino-1-methylindole-3-carboxylic Acid.** GEORG REIF (*Ber.*, 1909, 42, 3036—3045).—According to Piccinini and Salmonini (*Abstr.*, 1902, i, 491), it is not possible to transform indolecarboxylic acid into aminoindole by the Hofmann-Curtius reaction. It is now shown that an aminocarboxylic acid can be obtained by this reaction from 1-indole-2:3-dicarboxylic acid.

*Ethyl 1-methylindole-2:3-dicarboxylate*,  $C_6H_4 \begin{smallmatrix} \diagup C(CO_2H) \\ \diagdown NMe \end{smallmatrix} C \cdot CO_2H$ ,

is readily obtained by Fischer's method (*Abstr.*, 1886, 805) from the phenylmethylhydrazoné of ethyl oxalacetate, and can be purified by distillation in steam. It forms a reddish-brown oil, and has an obnoxious odour. When hydrolysed with 20% alcoholic potassium hydroxide, a precipitate of *potassium ethyl methylindoledicarboxylate*,  $CO_2K \cdot C_9H_7N \cdot CO_2Et$ , is formed. The acid ester,  $CO_2H \cdot C_9H_7N \cdot CO_2Et$ , crystallises from dilute alcohol in brilliant needles, has m. p. 158° (corr.) when heated quickly, and does not give the pine-wood reaction. The *dicarboxylic acid*,  $C_9H_7N(CO_2H)_2$ , obtained by hydrolysing the monopotassium salt with aqueous potassium hydroxide, crystallises from dilute alcohol in large prisms, and when heated quickly has m. p. 218° (corr.); at the same time carbon dioxide is evolved and 1-methylindole formed. The *acid chloride*,  $C_9H_7N(COCl)_2$ , prepared by shaking the acid with light petroleum and phosphorus pentachloride, crystallises from benzene in small needles; it turns yellow at 82°, melts at a higher temperature, and is readily decomposed by water. The *amide*,  $C_9H_7N(CO \cdot NH_2)_2$ , crystallises from hot water in slender needles with a silky lustre. When rapidly heated, it sinters at 259° and melts at 267° (decomp., corr.). The *ester of the amic acid*,



crystallises from benzene or light petroleum in long needles, m. p. 201° (decomp., corr.). The *anhydride*,  $C_9H_7N \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$ , obtained by the action of acetyl chloride or acetic anhydride on the acid, crystallises from ethyl acetate in large, glistening, rhombohedral prisms, sintering at 209° and melting at 212° (corr.). The *amic acid*,



obtained in the form of its *ammonium* salt by the action of ammonia on a benzene solution of the anhydride, crystallises in small prisms, m. p. 204° (decomp., corr.), and when its solution in sodium hydroxide is treated with sodium hypochlorite (Graebe, *Abstr.*, 1902, i, 663), it

yields an *acid product*,  $C_9H_7\begin{matrix} N=C\cdot OH \\ \diagup \\ CO\cdot O \end{matrix}$ , which crystallises from dilute acetone in slender, glistening needles, m. p.  $260^\circ$  (decomp.). This product, analogous to isatoic anhydride (Mohr, this vol. i, 420), dissolves readily in alkalis and ammonia, and when boiled with 5% sodium hydroxide solution yields 2-(or 3)amino-1-methylindole-3-(or 2)-carboxylic acid,  $NH_2\cdot C_9H_7N\cdot CO_2H$ , which crystallises from acetone in long needles, m. p.  $65-69^\circ$  (decomp., corr.), and is extremely unstable, rapidly changing colour in contact with the air. It gives a bluish-brown coloration with an aqueous bleaching powder solution, and its alcoholic solution gives a blue coloration with a few drops of ferric chloride. With *p*-dimethylaminobenzaldehyde, it gives a reddish-coloured additive compound analogous to the product obtained by Pawleski (Abstr., 1908, i, 638) from anthranilic acid. J. J. S.

**The Red Urinary Pigment Derived from Indole. II.** ALBERICO BENEDICENTI (*Zeitsch. physiol. Chem.*, 1909, 62, 390-398. Compare Abstr., 1908, ii, 1057).—It is shown that methylketole (2-methylindole), when administered to animals, does not pass in an unaltered condition into the urine, but is transformed into a chromogen, which yields a red pigment when oxidised with hydrochloric acid and calcium hypochlorite. The same chromogen appears to be formed when 2-methylindole is brought into contact with urine *in vitro*, and numerous other *O*-alkylated indoles behave in the same manner as 2-methylindole.

The pigment obtained by oxidising 2-methylindole with hydrochloric acid and hypochlorite has been investigated. The formation of the red compound is preceded by the production of a green coloration, which changes rapidly into the red compound unless the temperature is kept low. Most oxidising agents form the green compound as an intermediate substance, but ferric chloride appears to produce the red pigment directly.

The crude red compound is washed and dried, then extracted with hot benzene to remove methylindole, and finally dissolved in acetic acid and precipitated with water. The last traces of chlorine can only be removed by solution in alcohol and treatment with small amounts of sodium. The analyses of the purified product agree with the formula  $C_{12}H_{13}ON$ , and in many respects it resembles Niggeler's Indigo-red. It is not an oxidation product of indoxyl, and has phenolic properties. A dinitro-derivative,  $C_{12}H_{11}(NO_2)_2ON$ , has been obtained as a yellow, amorphous powder.

It is probable that the red compound is identical with the red pigment of urine. J. J. S.

**Acetylchloroacetyl tetrahydroquinoline.** FRANZ KUNCKELL and ERNST VOLLHASE (*Ber.*, 1909, 42, 3196-3199).—The work of one of the authors on the preparation of amino-ketones by means of the Friedel and Crafts reaction between chloroacetyl chloride and acylamines (Abstr., 1900, i, 664; 1901, i, 213) is now extended to tetrahydroquinoline and diphenylamine. The amines themselves do

not enter into the reaction, but their acetyl derivatives do so readily. Diphenylamine will form the subject of a further communication.

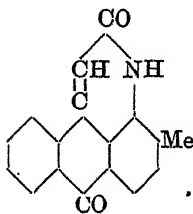
*Acetylchloroacetyltetrahydroquinoline*,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_5\text{OAc}$ , is obtained in a 60% yield, and forms white needles, which have m. p.  $137^\circ$ . *Acetylbromoacetyltetrahydroquinoline*, from bromoacetyl bromide and acetyltetrahydroquinoline, forms white, silky needles, m. p.  $134^\circ$ . To remove the acetyl group, the acetylchloroacetyltetrahydroquinoline was heated with 20% hydrochloric acid on the water-bath until dissolved; on neutralising with ammonium carbonate, *chloroacetyltetrahydroquinoline* was precipitated. It crystallises in yellow leaflets, which have m. p.  $123\text{--}124^\circ$ . A *hydrochloride* or *hydrobromide* of the compound could not be prepared. Oxidation of acetylchloroacetyltetrahydroquinoline with hydrogen peroxide yielded an *acetyltetrahydroquinolinecarboxylic acid*, which crystallises in small, yellowish-white needles, m. p.  $187^\circ$ .

*Acetylchloroacetyl-6-methyltetrahydroquinoline* crystallises in white needles, m. p.  $132^\circ$ . *Acetylbromoacetyl-6-methyltetrahydroquinoline* also forms white needles, m. p.  $128^\circ$ . R. V. S.

#### Action of Benzoyl Chloride on Hydroxyquinolines.

ALEXANDER ELLINGER and OTTO RIESER (*Ber.*, 1909, 43, 3336—3339). —When kynurine (4-hydroxyquinoline) or 2-hydroxy-4-methylquinoline (compare Knorr and Klotz, *Abstr.*, 1887, 278) is boiled for several hours with excess of benzoyl chloride, no benzoyl derivative is obtained, the reaction which occurs consisting in the substitution of the hydroxyl group by chlorine. Thus,  $\psi$ -hydroxyquinoline yields  $\psi$ -chloroquinoline, the platinichloride of which has m. p.  $280\text{--}281^\circ$  (Skraup, *Abstr.*, 1890, 174, gave m. p.  $278\text{--}279^\circ$ ). Similarly, 2-hydroxy-4-methylquinoline gives 2-chloro-4-methylquinoline, the platinichloride of which has m. p.  $55^\circ$  (Knorr, *loc. cit.*, gave  $59^\circ$ ); in this case, the yield is small, owing more to the presence of the methyl group than to the 2-position of the hydroxyl, since, under similar conditions, 4-hydroxy-2-methylquinoline gives only traces of a volatile base. T. H. P.

[Preparation of 2-Methylantrapyridone.]  
BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212204).  
—2-Methylantrapyridone (annexed formula) (yellow crystals from acetic acid) is prepared by heating together 1-acetylamino-2-methylantraquinone and acetic anhydride for half an hour at  $210^\circ$ . The halogenated aminoanthraquinones can also be employed for this condensation. The products are crystalline, soluble in the ordinary high boiling organic solvents, and the solutions show greenish-yellow fluorescence. F. M. G. M.



**Addition of Hydroxylamine to Acetylene Derivatives.**  
E. OLIVERI-MANDALÀ (*Atti R. Accad. Lincei*, 1909, [v], 13, ii, 141—144. Compare Claisen, *Abstr.*, 1904, i, 14; Ruhemann and Cunningham, *Trans.*, 1899, 778, 954).—The action of hydroxylamine on ethyl

yields an acid product,  $C_9H_7 \begin{smallmatrix} N=C\cdot OH \\ \diagup \\ CO\cdot O \end{smallmatrix}$ , which crystallises from dilute acetone in slender, glistening needles, m. p.  $260^\circ$  (decomp.). This product, analogous to isatoic anhydride (Mohr, this vol., i, 420), dissolves readily in alkalis and ammonia, and when boiled with 5% sodium hydroxide solution yields 2-(or 3)amino-1-methylindole-3-(or 2)-carboxylic acid,  $NH_2\cdot C_9H_7N\cdot CO_2H$ , which crystallises from acetone in long needles, m. p.  $65-69^\circ$  (decomp., corr.), and is extremely unstable, rapidly changing colour in contact with the air. It gives a bluish-brown coloration with an aqueous bleaching powder solution, and its alcoholic solution gives a blue coloration with a few drops of ferric chloride. With *p*-dimethylaminobenzaldehyde, it gives a reddish-coloured additive compound analogous to the product obtained by Pawleski (Abstr., 1908, i, 638) from anthranilic acid. J. J. S.

**The Red Urinary Pigment Derived from Indole. II.** ALBERICO BENEDICENTI (*Zeitsch. physiol. Chem.*, 1909, 62, 390-398. Compare Abstr., 1908, ii, 1057).—It is shown that methylketole (2-methylindole), when administered to animals, does not pass in an unaltered condition into the urine, but is transformed into a chromogen, which yields a red pigment when oxidised with hydrochloric acid and calcium hypochlorite. The same chromogen appears to be formed when 2-methylindole is brought into contact with urine *in vitro*, and numerous other *C*-alkylated indoles behave in the same manner as 2-methylindole.

The pigment obtained by oxidising 2-methylindole with hydrochloric acid and hypochlorite has been investigated. The formation of the red compound is preceded by the production of a green coloration, which changes rapidly into the red compound unless the temperature is kept low. Most oxidising agents form the green compound as an intermediate substance, but ferric chloride appears to produce the red pigment directly.

The crude red compound is washed and dried, then extracted with hot benzene to remove methylindole, and finally dissolved in acetic acid and precipitated with water. The last traces of chlorine can only be removed by solution in alcohol and treatment with small amounts of sodium. The analyses of the purified product agree with the formula  $C_{12}H_{13}ON$ , and in many respects it resembles Niggeler's Indigo-red. It is not an oxidation product of indoxyl, and has phenolic properties. A dinitro-derivative,  $C_{12}H_{11}(NO_2)_2ON$ , has been obtained as a yellow, amorphous powder.

It is probable that the red compound is identical with the red pigment of urine. J. J. S.

**Acetylchloroacetyltetrahydroquinoline.** FRANZ KUNCKELL and ERNST VOLLHASE (*Ber.*, 1909, 42, 3196-3199).—The work of one of the authors on the preparation of amino-ketones by means of the Friedel and Crafts reaction between chloroacetyl chloride and acylamines (Abstr., 1900, i, 664; 1901, i, 213) is now extended to tetrahydroquinoline and diphenylamine. The amines themselves do

not enter into the reaction, but their acetyl derivatives do so readily. Diphenylamine will form the subject of a further communication.

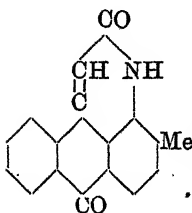
*Acetylchloroacetyltetrahydroquinoline*,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_9\text{NH}_2\text{OAc}$ , is obtained in a 60% yield, and forms white needles, which have m. p.  $137^\circ$ . *Acetylbromoacetyltetrahydroquinoline*, from bromoacetyl bromide and acetyltetrahydroquinoline, forms white, silky needles, m. p.  $134^\circ$ . To remove the acetyl group, the acetylchloroacetyltetrahydroquinoline was heated with 20% hydrochloric acid on the water-bath until dissolved; on neutralising with ammonium carbonate, *chloroacetyltetrahydroquinoline* was precipitated. It crystallises in yellow leaflets, which have m. p.  $123\text{--}124^\circ$ . A *hydrochloride* or *hydrobromide* of the compound could not be prepared. Oxidation of acetylchloroacetyltetrahydroquinoline with hydrogen peroxide yielded an *acetyltetrahydroquinolinecarboxylic acid*, which crystallises in small, yellowish-white needles, m. p.  $187^\circ$ .

*Acetylchloroacetyl-6-methyltetrahydroquinoline* crystallises in white needles, m. p.  $132^\circ$ . *Acetylbromoacetyl-6-methyltetrahydroquinoline* also forms white needles, m. p.  $128^\circ$ . R. V. S.

#### Action of Benzoyl Chloride on Hydroxyquinolines.

ALEXANDER ELLINGER and OTTO RIESER (*Ber.*, 1909, 43, 3336—3339).—When kynurine (4-hydroxyquinoline) or 2-hydroxy-4-methylquinoline (compare Knorr and Klotz, *Abstr.*, 1887, 278) is boiled for several hours with excess of benzoyl chloride, no benzoyl derivative is obtained, the reaction which occurs consisting in the substitution of the hydroxyl group by chlorine. Thus,  $\psi$ -hydroxyquinoline yields  $\psi$ -chloroquinoline, the platinichloride of which has m. p.  $280\text{--}281^\circ$  (Skraup, *Abstr.*, 1890, 174, gave m. p.  $278\text{--}279^\circ$ ). Similarly, 2-hydroxy-4-methylquinoline gives 2-chloro-4-methylquinoline, the platinichloride of which has m. p.  $55^\circ$  (Knorr, *loc. cit.*, gave  $59^\circ$ ); in this case, the yield is small, owing more to the presence of the methyl group than to the 2-position of the hydroxyl, since, under similar conditions, 4-hydroxy-2-methylquinoline gives only traces of a volatile base. T. H. P.

#### [Preparation of 2-Methylantrapyridone.]

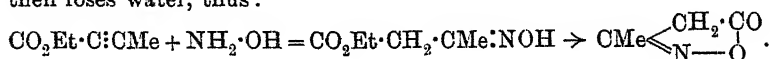


BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212204).—2-Methylantrapyridone (annexed formula) (yellow crystals from acetic acid) is prepared by heating together 1-acetylamino-2-methylantraquinone and acetic anhydride for half an hour at  $210^\circ$ . The halogenated aminoanthraquinones can also be employed for this condensation. The products are crystalline, soluble in the ordinary high boiling organic solvents, and the solutions show greenish-yellow fluorescence. F. M. G. M.

#### Addition of Hydroxylamine to Acetylene Derivatives.

E. OLIVERI-MANDALÀ (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 141—144. Compare Claisen, *Abstr.*, 1904, i, 14; Ruhemann and Cunningham, *Trans.*, 1899, 778, 954).—The action of hydroxylamine on ethyl

tetrolate in alcoholic solution rendered slightly alkaline with sodium hydroxide yields, as the sole separable product, the methylisooxazolone obtained by Hantzsch (Abstr., 1891, 739) by the action of an alkaline solution of hydroxylamine on ethyl acetoacetate. The first stage in the reaction consists in the addition of the hydroxylamine to the tetrolic ester with formation of ethyl oximinoacetoacetate, which then loses water, thus:



It is worthy of note that hydroxylamine is added to two carbon atoms united by a triple linking in the same manner as to a carbon atom and a nitrogen atom joined by a triple linking.

T. H. P.

**New Series of Leuco-bases and of Colouring Matters Derived from Diphenylethylene.** PAUL LEMOULT (*Compt. rend.*, 1909, 149, 606—608).—The alkyl derivatives of diphenylethylene described by Busignies (this vol., i, 736) are leuco-bases of the same type as the corresponding derivatives of diphenylmethane. In solutions acidified with acetic acid, they rapidly absorb oxygen from the air and develop distinctive colorations. By adding an alkali nitrite to an acidified solution of the base, intense colorations are obtained varying from green in the case of tetramethyl- and tetraethyl-diaminodiphenylethylene to blue in the case of the corresponding propylene derivatives. The dialkylmonoamino-bases give orange-yellow solutions under these conditions. When dyed on cotton mordanted with tannin, the shades produced resemble those obtained with derivatives of di- or tri-phenylmethane.

The author considers the development of the colouring matter to be due, not to decomposition of the bases, but to their specific constitution.

W. O. W.

**Hydrazine Derivatives of Triphenylmethane. Constitution of Triphenylmethyl.** HEINRICH WIELAND (*Ber.*, 1909, 42, 3020—3030).—In spite of the use of all manner of oxidising agents it was not found possible to convert hydrazotriphenylmethane into azotriphenylmethane,  $\text{CPh}_3\cdot\text{N}:\text{N}\cdot\text{CPh}_3$ . It appears that azotriphenylmethane, even at  $0^\circ$ , spontaneously dissociates into nitrogen and triphenylmethyl. The latter was isolated as triphenylmethyl peroxide with a yield of 60%, or as the perhaloids of  $\omega$ -bromo- or  $\omega$ -iodotriphenylmethane when bromine or iodine were used as oxidising agents.

**Hydrazotriphenylmethane**,  $\text{CPh}_3\cdot\text{NH}\cdot\text{NH}\cdot\text{CPh}_3$ , prepared by the action of hydrazine hydrate on  $\omega$ -chlorotriphenylmethane, forms long, colourless, glistening, rectangular plates, m. p.  $209^\circ$  (partial decomp.). It dissolves in sulphuric acid with an orange-yellow coloration. It is readily reduced, but remarkably stable towards atmospheric oxygen or mild oxidising agents; more powerful oxidising agents convert it into triphenylmethyl.

**Triphenylmethylhydrazine**,  $\text{CPh}_3\cdot\text{NH}\cdot\text{NH}_2$ , is formed at the same time as the hydrazo-compound; the hydrochloride crystallises in colourless, rhombic plates, m. p.  $133^\circ$ . The free base crystallises only with difficulty in needles, m. p.  $108\text{--}112^\circ$  (decomp.), and readily decomposes

when boiled in solvents; the *acetate* separates in stellar aggregates of colourless needles, m. p. 197° (decomp.).

By the reduction of triphenylmethylhydrazine with sodium nitrite, *triphenylmethylazoimide*,  $\text{CPh}_3 \cdot \text{N} < \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$ , is formed. This crystallises very well in large, colourless, dice-like rhombohedra, m. p. 64°, decomp. 180°. This azoimide is very stable; it dissolves in concentrated sulphuric acid with a golden-yellow colour, and is not affected by boiling with water.

Schmidlin (Abstr., 1908, i, 150) has shown that triphenylmethyl exists in a colourless and a coloured form. In solution the colourless form in part passes over into the yellow isomeride; equilibrium exists between the two forms, the proportion of each being dependent on the temperature and the nature of the solvent. It is claimed that the yellow isomeride possesses the true triphenylmethyl structure. Gomberg's molecular-weight determinations indicated the double molecular weight, but applied to solutions in which not more than about 5% of the yellow isomeride can have been present. In naphthalene, however, where the amount of the yellow unimolecular form is much larger, a much lower molecular weight was found.

E. F. A.

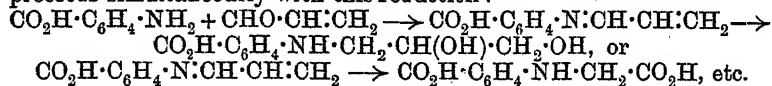
**Mobility of the Amino-group.** GALEAZZO PICCININI (*Ber.*, 1909, 42, 3219—3233).—In a former paper (Abstr., 1908, i, 908) the author has described two amino-bases, 3-amino-2-keto-4:6:6-trimethyltetrahydropyridine and 3-amino-2-keto-1:4:6:6-tetramethyltetrahydropyridine, which, when acted on with water at the ordinary temperature, exchange the group  $-\text{NH}_2$  for  $-\text{OH}$ . A similar looseness of the carbon-nitrogen linking can be observed in most compounds of the type  $\text{R} \cdot \text{C}(\text{NH}_2) \cdot \text{E}$ , where E may be any negative element of valency greater than one. In order to compare the mobility of the amino-group in different compounds, it is necessary to follow carefully the hydrolysis in the different cases to obtain a measure of the influence of substituents, etc. To this end the reaction has been followed by physical-chemical methods in the case of the above compounds.

The method adopted was to enclose known quantities of the base and water in sealed tubes in a thermostat at 25°. At intervals a tube was removed and the amount of ammonia which had been formed was estimated. In aqueous solution at 25° the conversion of amine into hydroxy-compound reached an equilibrium when the ammonia formed was not removed. The reversibility of the reaction was further shown by the preparation of one of the bases, 3-amino-2-keto-4:6:6-trimethyltetrahydropyridine, from the corresponding hydroxy-compound by the action of aqueous or alcoholic ammonia. Alkali hydroxides do not affect the course of the reaction. In acid solution (hydrochloric acid) the reaction is greatly accelerated; the hydrochlorides decompose completely, even in dilute solution, according to the formula for unimolecular reactions which proceed completely. The constant of the reaction is greatest when the concentration is 1—2 gram-molecules of hydrochloride per litre.

When the amount of acid in the solution is increased above the equivalent quantity, the value of the reaction constant decreases, whatever the concentration of the hydrochloride in the solution. The reaction constant is increased by rise of temperature:  $K$  at  $50^\circ/K$  at  $25^\circ=10$ ;  $K$  at  $100^\circ/K$  at  $25^\circ=100$ . The *N*-methylated base is the more quickly hydrolysed. The author considers that the observed influence of change of concentration, alkali, acid, etc., on the progress of the reaction receives a satisfactory explanation if it is supposed that the hydrolysis is a hydrolysis of the ion of the base, and not of the undissociated molecules themselves. In this connexion, experiments in other solvents are to be undertaken. A similar study of the nitroanilines and of picramide is also in progress. R. V. S.

**Mechanism of the Formation of Indigotin from Anthranilic Acid and Polyhydroxy-compounds. New Synthesis of Indigotin.** IWAN VON OSTROMISLENSKY and A. PAMFILOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 784—789).—The mechanism of the formation of indigotin by heating anthranilic acid with potassium hydroxide in presence of glycerol may be explained by the following scheme:  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} + \text{C}_3\text{H}_5(\text{OH})_3 \rightarrow$   
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH} \rightarrow$   
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H} \rightarrow$   
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \rightarrow$   
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \rightarrow \text{C}_6\text{H}_4 \langle \text{NH} \rangle \text{CH}_2 \rightarrow \text{indigotin}.$

When acraldehyde is employed in place of glycerol, the reduction of the group  $\cdot\text{N}:\text{CH}\cdot$  to  $\cdot\text{NH}\cdot\text{CH}_2\cdot$  is effected by the hydrogen always formed in oxidation processes brought about by potassium hydroxide, owing to the dissociation of water, this hydrogen, in a nascent state, acting on the initial products of the process; oxidation of  $\cdot\text{CH}:\text{CH}_2$  proceeds simultaneously with this reduction:



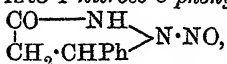
According to the above views, it should be possible to prepare indigotin from *o*-aminobenzyl alcohol, the group  $\text{CH}_2\cdot\text{OH}$  undergoing oxidation to  $\text{CO}_2\text{H}$ ; this the authors find to be the case. A mixture of *o*-aminobenzyl alcohol, potassium hydroxide, and glycerol, heated in an atmosphere of nitrogen to  $280\text{--}300^\circ$ , yields indigotin, the amount of which is increased on passing air through the mixture; the yield is appreciably greater than that obtained under the same conditions from anthranilic acid, and, as the indigotin begins to form in about two minutes, the reaction may serve as a lecture experiment. As *o*-aminobenzyl alcohol has b. p.  $270\text{--}280^\circ$ , the yield of indigotin would doubtless be increased if the heating were carried out in a reflux apparatus, or, better still, an autoclave.

T. H. P.

**Formation of Nitrosopyrazolidones and Pyrazolones from Hydrazides of Unsaturated Acids.** ERNST MUCKERMANN (*Ber.*, 1909, 42, 3449—3460).—*Cinnamoyl hydrazide*,  
 $\text{CHPh}:\text{CH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ ,

m. p. 101°, is obtained by the prolonged heating of ethyl cinnamate, alcohol, and hydrazine hydrate. With alcoholic hydrogen chloride at 0°, it forms a *hydrochloride*,  $C_9H_{10}ON_2 \cdot HCl$ , m. p. 201° (decomp.), whilst with benzaldehyde it yields the *benzylidene* derivative,

$C_{16}H_{14}ON_2$ ,  
m. p. 180°. An aqueous solution of the hydrochloride at 0° is converted by sodium nitrite into 1-nitroso-5-phenyl-3-pyrazolidone,



m. p. 127—128° (decomp.), which responds to Liebermann's reaction, is very soluble in alkalis, yields heavy precipitates with many metallic salts, is converted by bromination in acetic acid into Rothenburg's 4:4-dibromo-3-phenyl-5-pyrazolone (m. p. 198°, not 189°), yields cinnamic acid by treatment with boiling concentrated hydrochloric acid, and Rothenburg's 4-oximino-3-phenyl-5-pyrazolone with boiling dilute sulphuric acid.

*Crotonyl hydrazide*,  $CHMe \cdot CH \cdot CO \cdot NH \cdot NH_2$ , is a syrup which is obtained in a similar way, and yields a similar series of derivatives. The *hydrochloride* has m. p. 173° (decomp.), and the *benzylidene* compound, m. p. 72°. 1-Nitroso-5-methyl-3-pyrazolidone, m. p. 131° (decomp.), closely resembles the corresponding phenyl derivative in its preparation and properties. C. S.

**Bromination of Diphenylglyoxalone.** HEINRICH BILTZ (*Annalen*, 1909, 368, 262—270. Compare Abstr., 1908, i, 573, 575).—A solution of 4:5-diphenylglyoxalone in concentrated sulphuric acid, when treated with bromine and kept in a desiccator, deposits 4:5-di-p-bromophenylglyoxalone disulphate,  $C_{15}H_{10}ON_2Br_2 \cdot 2H_2SO_4$ , as colourless, hexagonal prisms, m. p. 70—80°, which, when boiled with water, yields 4:5-di-p-bromophenylglyoxalone. By using certain proportions of the reagents and pouring the solution on to ice, it is possible to obtain good yields of 4:5-dihydroxy-4:5-diphenyldihydroglyoxalone (*loc. cit.*), which forms slender, flexible needles, m. p. 250° (decomp.). W. H. G.

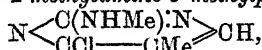
**Pyrimidines. XLVI. Dimethyl Derivatives of 2-Aminopyrimidine.** Preparation of 2-Methylamino-5-methylpyrimidine. TREAT B. JOHNSON and KENNETH G. MACKENZIE (*Amer. Chem. J.*, 1909, 42, 353—370).—Suzuki, Aso, and Mitarai (*Bull. Coll. Agric. Tōkyō*, 1907, 7, 477), in an investigation of the constituents of soja source, have described two products of the composition  $C_6H_9N_3$  and  $C_4H_{12}N_3$ , and have stated that the former compound is probably an amino-dimethylpyrimidine.

The present authors are making a study of the pyrimidines of the formula  $C_6H_9N_3$ , and have now described 2-methylamino-5-methylpyrimidine and some derivatives of 2-methylamino-4-methylpyrimidine. It has been pointed out by Johnson (Abstr., 1907, i, 879) that when 2-methylthiol-5-methyl-6-pyrimidone-4-carboxylic acid, obtained by the condensation of  $\psi$ -methylthiocarbamide with the sodium derivative of ethyl oxalylpropionate, is heated above its m. p., it is converted into 2-methylthiol-5-methyl-6-pyrimidone. It is now shown that this

compound, on hydrolysis, gives a quantitative yield of thymine, and the investigation has been extended.

2-Methylamino-5-methyl-6-pyrimidone,  $\text{NH} \begin{smallmatrix} \text{C}(\text{NHMe})\text{:N} \\ \text{CO} \text{---} \text{CMe} \end{smallmatrix} \text{CH}$ , m. p. 213°, obtained by the action of methylamine on 2-methylthiol-5-methyl-6-pyrimidone, forms colourless crystals containing  $1\text{H}_2\text{O}$ , and gives a claret-red colour with diazobenzenesulphonic acid in presence of sodium hydroxide. The *sulphate* melts at 202°, and the *picrate* at 240° (decomp.); the *platinichloride* was also prepared.

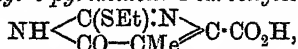
When 2-methylamino-5-methyl-6-pyrimidone is heated with phosphoryl chloride, 6-chloro-2-methylamino-5-methylpyrimidine,



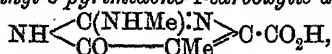
m. p. 131°, is produced, which forms prismatic crystals, sublimes at 100°, and when treated with zinc dust is converted into 2-methylamino-5-methylpyrimidine,  $\text{N} \begin{smallmatrix} \text{C}(\text{NHMe})\text{:N} \\ \text{CH} \text{---} \text{CMe} \end{smallmatrix} \text{CH}$ , m. p. 102°, which crystallises in prisms, and is not identical with the base obtained by Suzuki, Aso, and Mitarai (*loc. cit.*). 2-Methylamino-5-methylpyrimidine does not give an immediate coloration on addition of diazobenzenesulphonic acid, but, after a time, a deep red colour is developed; its *picrate* does not melt, but decomposes above 150°; the *hydrochloride*, m. p. 162—163°, crystallises in prisms.

2-Methylamino-4-methyl-6-pyrimidone (Jaeger, Abstr., 1891, 1007), m. p. 201—202°, has been prepared by heating 2-methylthiol-4-methyl-6-pyrimidone with excess of methylamine at 140—150°. When this compound is heated with phosphoryl chloride, 6-chloro-2-methylamino-4-methylpyrimidine,  $\text{N} \begin{smallmatrix} \text{C}(\text{NHMe})\text{:N} \\ \text{CCl} \text{---} \text{CH} \end{smallmatrix} \text{CMe}$ , m. p. 135°, is produced, which forms colourless needles, and slowly sublimes above 100°. If this chloropyrimidine is treated with zinc dust, a double compound of 2-methylamino-4-methylpyrimidine and zinc chloride,  $2\text{C}_6\text{H}_5\text{N}_3\cdot\text{ZnCl}_2$ , m. p. 170—172°, is produced, which forms red crystals. The presence of 2-methylamino-4-methylpyrimidine in the reaction product was established by means of the *picrate*, m. p. 150—155°, which forms irregular prisms.

2-Ethylthiol-5-methyl-6-pyrimidone-4-carboxylic acid,



m. p. 220°, obtained by the condensation of  $\psi$ -ethylthiocarbamide with the sodium derivative of ethyl methylloxalacetate, forms needles or prisms; the *ethyl ester*, m. p. 172—173°, crystallises in prisms. If 2-ethylthiol-5-methyl-6-pyrimidone-4-carboxylic acid is heated at 220—230°, it undergoes decomposition with formation of 2-ethylthiol-5-methyl-6-pyrimidone (Wheeler and Johnson, Abstr., 1904, i, 624), which, when heated with concentrated hydrochloric acid for several hours, is converted into thymine. By the action of methylamine on 2-ethylthiol-5-methyl-6-pyrimidone-4-carboxylic acid at 140—150°, 2-methylamino-5-methyl-6-pyrimidone-4-carboxylic acid,

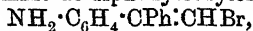


m. p. 270—280° (decomp.), is produced, which forms long, slender crystals. The *hydrochloride* crystallises in prisms and decomposes at 276—283°; the *methylamine* salt forms granular crystals, and decomposes at 274°. E. G.

**New Synthesis of Cinnoline Derivatives.** RICHARD STOERMER and H. FINCKE (*Ber.*, 1909, 42, 3115—3132. Compare von Richter, *Abstr.*, 1883, 1105; Busch and Klett, *ibid.*, 1892, 1494; Busch and Rast, 1897, i, 300).—When attempts are made to replace by hydroxyl the amino-groups in certain *o*-amino-*as*-diphenylethylene derivatives, almost quantitative yields of cinnoline derivatives are obtained in the form of salts:

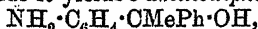


When  $\alpha$ -bromo- $\beta$ -*o*-amino-*as*-diphenylethylene,

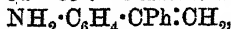


is used, phenylcinnoline and not a bromo-derivative is formed. *o*-Aminodiphenylmethylcarbinol,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPhMe} \cdot \text{OH}$ , does not yield a cinnoline derivative.

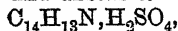
*o*-Aminobenzophenone is best prepared by a modification of Ullmann and Bleier's method (*Abstr.*, 1903, i, 176). When condensed with magnesium methyl iodide it yields *o*-aminodiphenylmethylcarbinol,



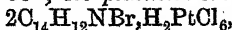
which crystallises from a mixture of benzene and light petroleum in colourless prisms, m. p. 84—85°. *o*-Amino-*as*-diphenylethylene,



obtained by boiling the carbinol for one hour with 35% sulphuric acid, forms colourless crystals, m. p. 76—77.5°. The *hydrochloride* is sparingly soluble; the *platinichloride* melts and decomposes at 195°, and the *aureichloride* is oily and unstable. The *sulphate*,

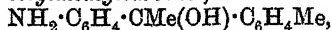


forms sparingly soluble, pale yellow, crystalline plates, m. p. 166—168°; the *picrate*,  $\text{C}_{20}\text{H}_{16}\text{O}_7\text{N}_4$ , forms brilliant, yellow crystals, m. p. 149°, and the *acetyl* derivative, which can be obtained either from the olefine directly or by heating the carbinol for some time with sodium acetate and acetic anhydride, separates from alcohol in colourless crystals, m. p. 122°. *o*-Acetylaminodiphenylmethylcarbinyl acetate,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CMePh} \cdot \text{OAc}$ , forms colourless crystals, m. p. 160—162°.  $\alpha$ -Bromo- $\beta$ -*o*-acetylaminodiphenylethylene,  $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh:CHBr}$ , obtained by the action of an acetic acid solution of bromine on acetylaminodiphenylethylene, separates from alcohol in colourless crystals, m. p. 146°, and when hydrolysed with fuming hydrochloric acid yields  $\alpha$ -bromo- $\beta$ -*o*-aminodiphenylethylene,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh:CHBr}$ , as colourless crystals, m. p. 87—88°; its *platinichloride*,



has m. p. 209° (decomp.).

*o*-Aminophenyl-*p*-tolylmethylcarbinol,

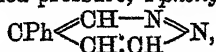


forms colourless crystals, m. p. 92—93°, and *o*-aminophenyl-*p*-tolylethylene,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C(C}_6\text{H}_4\text{Me)} \cdot \text{CH}_2$ , is an oil, b. p. 224—226°/50 mm. The *sulphate*,  $2\text{C}_{15}\text{H}_{15}\text{N}_2\text{H}_2\text{SO}_4$ , forms colourless plates, m. p.

141—142°. *o*-Aminodiphenylethylcarbinol,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{Et})\text{Ph} \cdot \text{OH}$ , obtained from *o*-aminobenzophenone and magnesium ethyl iodide, crystallises from alcohol in colourless plates, m. p. 101—102°, and when boiled with 30% sulphuric acid yields *o*-aminodiphenylpropylene,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} : \text{CHMe}$ , which separates from light petroleum as colourless crystals, m. p. 50—52°. The *hydrochloride*,  $\text{C}_{15}\text{H}_{15}\text{N} \cdot \text{HCl}$ , formed colourless plates, m. p. 205—208°; the *platinichloride* forms yellow crystals, m. p. 191° (decomp.), and the *aurichloride*, a red, crystalline powder, m. p. 125° (decomp.).

4-Phenylcinnoline,  $\text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{N}=\text{N} \\ \diagup \quad \diagdown \\ \text{CPh} \cdot \text{CH} \end{smallmatrix}$ , is obtained as its hydrochloride when a solution of *o*-aminodiphenylethylene in hydrochloric acid is diazotised at the ordinary temperature. The base, liberated by the action of ammonia on the salt, crystallises from light petroleum in sulphur-yellow, glistening prisms, m. p. 67—67.5°. The *hydrochloride*,  $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , forms yellow crystals, m. p. 130° (decomp.), and the *hydrobromide*, pale yellow, glistening crystals, m. p. 202—204°. The *basic hydriodide*,  $2\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{HI}$ , forms dark orange-coloured needles, m. p. 93—95°; its solutions in water, alcohol, and ether have a pale yellow colour, whereas those in chloroform have a reddish-brown colour. The *normal hydriodide*,  $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{HI}$ , forms well-developed, red crystals, which decompose at 150°. The *sulphate*,  $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{H}_2\text{SO}_4$ , forms golden-yellow crystals, m. p. 181—182°; the *nitrate*, pale yellow needles, m. p. 156—157°; the *picrate*,  $\text{C}_{20}\text{H}_{12}\text{O}_7\text{N}_5$ , deep golden-yellow, felted needles from benzene, m. p. 156—158° after sintering at 147—148°, and the *platinichloride*,  $2\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$ , pale brown crystals which are not molten at 300°. The *normal aurichloride*,  $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{HAuCl}_4$ , forms a sparingly soluble, pale yellow powder sintering at 158°; a second *aurichloride*,  $2\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{H}_2\text{AuCl}_6$ , forms golden-yellow, glistening crystals, m. p. 145—147°. The *argentinitrate*,  $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{AgNO}_3$ , crystallises from alcohol in slender, yellow plates, m. p. 260° (decomp.); the *methiodide*,  $\text{C}_{14}\text{H}_{10}\text{N}_2 \cdot \text{MeI}$ , crystallises from methyl alcohol in brilliant, red, glistening needles, which decompose at 220°, and the *methochloride*, in pale yellow plates, which begin to decompose at 70°.

When oxidised with hot permanganate solution, the phenylcinnoline yields 4-phenylpyridazine-5:6-dicarboxylic acid (4-phenylcinnolinic acid),  $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{CO}_2\text{H}) \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CPh} = \text{CH} \end{smallmatrix} \text{N}$ , which crystallises from dilute nitric acid in colourless needles containing  $1\text{H}_2\text{O}$ , and m. p. 220—221° (decomp.). It forms a *normal silver salt*,  $\text{C}_{12}\text{H}_6\text{O}_4\text{N}_2\text{Ag}_2 \cdot \text{H}_2\text{O}$ , an *acid silver salt*,  $3\text{C}_{12}\text{H}_6\text{O}_4\text{N}_2\text{Ag}_2 \cdot \text{C}_{12}\text{H}_6\text{O}_4\text{N}_2$ , and a *barium salt*,  $\text{C}_{12}\text{H}_6\text{O}_4\text{N}_2\text{Ba}$ . When heated during four hours at 125°, the dibasic acid yields 4-phenylpyridazine-5-carboxylic acid,  $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{CH} - \text{N} \\ \diagup \quad \diagdown \\ \text{CPh} : \text{CH} \end{smallmatrix} \text{N}$ , which crystallises from alcohol and melts at 220—221° (decomp.). When either of the acids is distilled under diminished pressure, 4-phenylpyridazine,



is obtained; it separates from light petroleum in colourless crystals, m. p. 86—86.5°.

The *platinichloride*,  $2\text{C}_{10}\text{H}_8\text{N}_2, \text{H}_2\text{PtCl}_6, \text{H}_2\text{O}$ , forms a yellow, flesh-coloured precipitate, m. p.  $295\text{--}300^\circ$  (decomp.).

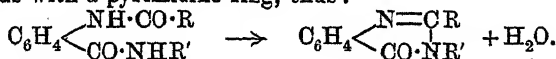
*p-Tolylcinnoline*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}=\text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{C}_7\text{H}_7):\text{CH} \end{smallmatrix}$ , obtained from *o*-aminophenyl-*p*-tolylethylene, crystallises from light petroleum in yellow prisms, m. p.  $58\text{--}59^\circ$ . The *nitrate* and *hydrochloride* are sparingly soluble, but the *sulphate* is readily soluble in water.

*4-Phenyl-3-methylcinnoline*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}=\text{N} \\ \diagup \quad \diagdown \\ \text{CPh}:\text{CMe} \end{smallmatrix}$ , forms pale, yellowish-brown crystals, m. p.  $135\text{--}136^\circ$ . Its salts are rather more soluble than those of phenylcinnoline. The *platinichloride*,

$2\text{C}_{15}\text{H}_{12}\text{N}_2, \text{H}_2\text{PtCl}_6$ , forms yellowish-brown plates, which decompose at about  $180^\circ$ .

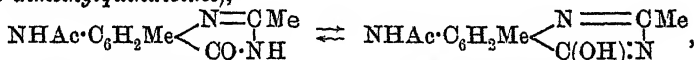
*4-Phenyl-3-methylcinnolinic acid*,  $\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_2, \text{H}_2\text{O}$ , forms colourless crystals, m. p.  $228\text{--}229^\circ$  (decomp.). J. J. S.

**Quinazolines. XXIII. 7-Amino-6-methylquinazolones, 7-Nitroquinazolone-6-carboxylic Acids, and 1:3:7:9-Naphthotetrazines.** MARSTON T. BOGERT and ALFRED H. KROPPF (*J. Amer. Chem. Soc.*, 1909, 31, 1071—1078).—The authors have previously described (this vol., i, 583) some amino- and nitroamino-derivatives of benzoic, *m*-toluic, and isophthalic acids containing an amino-group adjacent to a carboxyl group. The present paper gives an account of some quinazoline condensations of these acids, depending on the intermediate formation of acylantranilamides, which lose water and form compounds with a pyrimidine ring, thus:



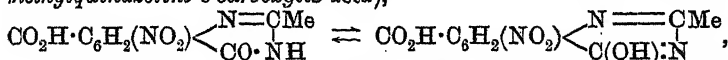
The intermediate amides have not been isolated.

*7-Acetylamino-2:6-dimethyl-4-quinazolone* (*7-acetylamino-4-hydroxy-2:6-dimethylquinazoline*),



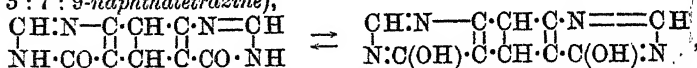
m. p. about  $330^\circ$ , obtained by the action of ammonium hydroxide on 2-acetylamino-1-methyl-4:5-acetylanthranil, forms colourless needles, and when boiled with potassium hydroxide is converted into *7-amino-2:6-dimethyl-4-quinazolone*, m. p. above  $300^\circ$ . *7-Acetylamino-3-phenyl-2:6-dimethyl-4-quinazolone*,  $\text{NHAc}\cdot\text{C}_6\text{H}_2\text{Me} \begin{smallmatrix} \text{N}=\text{CMe} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{NPh} \end{smallmatrix}$ , m. p.  $271^\circ$  (uncorr.), obtained by heating the acetylanthranil with aniline, crystallises in diamond-shaped plates.

*7-Nitro-2-methyl-4-quinazolone-6-carboxylic acid* (*7-nitro-4-hydroxy-2-methylquinazoline-6-carboxylic acid*),

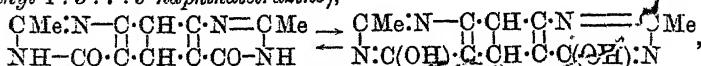


m. p. above  $300^\circ$ , obtained by boiling 4-nitroacetylanthranil-5-carboxylic acid with dilute ammonium hydroxide, forms colourless needles. *7-Nitro-3-phenyl-2-methyl-4-quinazolone-6-carboxylic acid*, m. p.  $315^\circ$  (uncorr.), prepared by the action of aniline on 4-nitroacetylanthranil-5-carboxylic acid, crystallises in yellow prisms.

4 : 6-Diketotetrahydro-1 : 3 : 7 : 9-naphthatetrazine (4 : 6-dihydro-1 : 3 : 7 : 9-naphthatetrazine),



m. p. above 310°, obtained by heating diethyl 4 : 6-diaminoisophthalate with formamide, forms a reddish-yellow powder. 4 : 6-Diketo-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine (4 : 6-dihydroxy-2 : 8-dimethyl-1 : 3 : 7 : 9-naphthatetrazine),

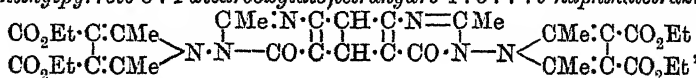


m. p. above 310°, prepared by the action of alcoholic ammonia on ethyl 4 : 6-diacetylaminoisophthalate, forms a pale yellow, amorphous powder; it can be obtained in better yield by boiling the bisacetanthranil from 4 : 6-diaminoisophthalic acid with dilute ammonium hydroxide. 4 : 6-Diketo-2 : 3 : 7 : 8-tetramethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine,

$\begin{array}{c} \text{CMe:N} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{N} = \text{CMe} \\ \text{NMe} \cdot \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CO} \cdot \text{NMe} \end{array}$  m. p. above 350°, obtained by heating the bisacetanthranil with aqueous methylamine,

forms long, colourless needles. 4 : 6-Diketo-2 : 8-dimethyl-3 : 7-dipropyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine, m. p. 220° (uncorr.), crystallises in small, lustrous needles. 4 : 6-Diketo-3 : 7-diphenyl-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine, m. p. 315°, prepared by heating the bisacetanthranil with aniline, forms minute, colourless needles. 4 : 6-Diketo-3 : 7-di-β-naphthyl-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine, m. p. 304° (uncorr.), crystallises in fluorescent needles.

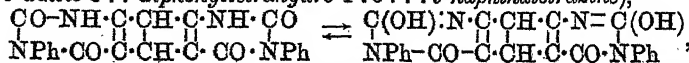
147—7-Diamino-4 : 6-diketo-2 : 8-dimethyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine, obtained by the action of hydrazine hydrate on the bisacetanthranil, forms yellow, nacreous scales; the hydrochloride, m. p. above 360° (decomp.), crystallises in colourless prisms; the diacetyl derivative, m. p. above 360°, forms small, colourless needles; the dibenzylidene derivative, m. p. above 350°, crystallises in granular form. When this diamidonaphthatetrazine is boiled with ethyl diacetylsuccinate dissolved in glacial acetic acid, 4 : 6-diketo-2 : 8-dimethyl-3 : 7-di(ethyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate)tetrahydro-1 : 3 : 7 : 9-naphthatetrazine,



m. p. 268.2° (corr.), is produced, which forms colourless needles or prisms. 3 : 7-Diphenylamino-4 : 6-diketo-2 : 8-dimethyltetrahydro-

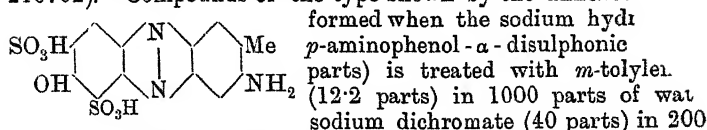
1 : 3 : 7 : 9-naphthatetrazine,  $\begin{array}{c} \text{CMe} \cdot \text{N} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{N} = \text{CMe} \\ \text{N(NHPh)} \cdot \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{C} \cdot \text{CO} \cdot \text{N} \cdot \text{NHPh} \end{array}$

m. p. above 320°, prepared by the action of phenylhydrazine on the bisacetanthranil, is a colourless, granular solid. 2 : 4 : 6 : 8-Tetraketo-3 : 7-diphenyloctahydro-1 : 3 : 7 : 9-naphthatetrazine (2 : 8-dihydroxy-4 : 6-diketo-3 : 7-diphenyltetrahydro-1 : 3 : 7 : 9-naphthatetrazine),



m. p. above 300°, obtained by heating diethyl 4 : 6-diphenyluraminoisophthalate with aniline at 225°, is a colourless, amorphous solid. E. G.

[Preparation of Substituted Azines.] CARL J. 210702).—Compounds of the type shown by the annexed

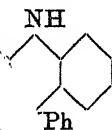


formed when the sodium hydroxide of *p*-aminophenol- $\alpha$ -disulphonic parts) is treated with *m*-tolylene (12.2 parts) in 1000 parts of water and sodium dichromate (40 parts) in 200 of water stirred in at the ordinary temperature. A dark precipitate separates, the mixture is heated with steam until a blood coloration appears, filtered, and the soluble dye salted out. *m*-Tolenediamine can be replaced by other *m*-diamines and the sodium dichromate by manganese dioxide. F. M. G. M.

**Remarks on Dihydroazines.** OSCAR HINSBERG (*Ber.*, 1909, 43, 3333—3336).—The statement made by Freund and Richard (this vol., i, 417) that *N*-phenyl- $\alpha$ -benzyl dihydrophenanthraquinazine is a yellow compound yielding red salts contradicts to some extent the observation of Hinsberg and Garfunkel (*Abstr.*, 1897, i, 123), who describes the mother substance of the above compound, *as-N*-phenyl dihydrophenanthraquinazine, as an almost colourless compound not forming coloured salts. The author finds that the latter compound forms faint yellow prisms or needles, m. p. 231—232° (m. p. previously given as 230°), and is neither coloured by concentrated hydrochloric acid nor altered by boiling for five minutes with acetic anhydride; if,

however, the boiling is prolonged for several hours, a *monoacetyl* derivative,  $C_{23}H_{20}ON$ , crystallising from alcohol in colourless needles, m. p. 196—197°, is obtained. The dihydroazine is hence only relatively stable towards acetic anhydride, and is to be regarded as *s-N*-phenyl dihydrophenanthraquinazine (annexed formula).

These results are in agreement with those of Richard (*loc. cit.*), the colourless benzyl derivative of the almost colourless *s-N*-phenyl dihydrophenanthra-



It is drawn that acetylation is insufficient to determine whether a dihydroazine belongs to the *s*- or *as*-series.

It may be assumed that also the non-alkylated dihydroazines, or at least the complex ones, of the *as*-series and their salts exhibit yellow or red colours, whilst those of the *s*-series are colourless (compare Freund and Richard, *loc. cit.*). T. H. P.

**Decomposition of the Leucosulphonic Acids of Rosaniline Hydrochloride and Crystal-Violet in Aqueous Solution.** JOSEPH H. KASTLE (*Amer. Chem. J.*, 1909, 42, 293—300).—It has been shown in an earlier paper (*Abstr.*, 1905, ii, 154) that the relative strengths of acids can be determined colorimetrically by means of solutions of certain vegetable colouring matters which have been bleached with sulphur dioxide. Unfortunately, such reagents are unstable, and must be freshly prepared from time to time, and the materials employed are only obtainable at certain seasons. A search has therefore been made for an artificial dye, the sulphurous

ative of which is decomposed by acids with regeneration of colour, but without success. In the course of this work, it has been found that when the leuco-sulphonic acids of rosaniline hydrochloride and its analogues are heated, they rapidly become coloured, but become colourless again on cooling. A number of experiments are described which lead to the conclusion that this behaviour is not due to dissociation of the air, but to dissociation, either simple or hydrolytic. It is pointed out that these colour changes form a striking lecture experiment to illustrate reversible actions.

E. G.

**A New Class of Dyes of Biochemical Importance.** Tri-indylmethane dyes. ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1909, 62, 276—286. Compare Ellinger, Abstr., 1906, i, 696).—The dye, obtained by boiling 3-indolealdehyde with dilute sulphuric acid, crystallises from glacial acetic acid in long, red needles, with a green metallic lustre resembling magenta. It is hygroscopic, and when heated at 130—140° has the composition  $2C_{25}H_{17}N_3 \cdot 3H_2SO_4$ . It sinters at 212°, and at higher temperatures decomposes slowly.

The product obtained when hydrochloric acid is used has the composition  $C_{25}H_{17}N_3 \cdot HCl$ . These dyes appear to be derived from tri-indylmethane,  $CH(C_8H_6N)_3$ , and to be analogous to the basic triphenylmethane dyes.

The same dye can be synthesised by heating oxalic or formic acid with indole and sulphuric acid, or, even better, by boiling the product formed from the action of alcoholic potassium hydroxide and form on indole with sulphuric acid.

When the dye base is heated with water at 220°, it yields 3-indolealdehyde.

Dyes can also be obtained by condensing indolealdehyde with various derivatives, for example, scatole, indolecarboxylic acid, etc.

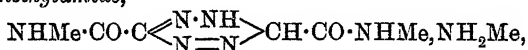
Urorosein is probably a tri-indylmethane dye (Herter, *ibid.*, 410).

**Alkylamides of 3:4-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylic Acid and 1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylic Acid.** ERNST MÜLLER (*Ber.*, 1909, 42, 3270—3284. Compare Curtius, Darapsky, and Müller, Abstr., 1908, i, 924).—An investigation on the action of methylamine, ethylamine, heptylamine, dimethylamine, diethylamine, and piperidine on ethyl diazoacetate. It is found that the alkylamines which most closely resemble ammonia, namely, the lower primary alkylamines, react fairly readily with ethyl diazoacetate, yielding alkylamine salts of 3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylalkylamides together with small quantities of the corresponding 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylalkylamides, whilst, probably because of the slow rate with which the reaction proceeds, only derivatives of 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylic acid are formed by the action of heptylamine, dimethylamine, and

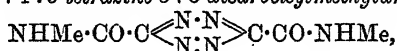
piperidine on ethyl diazoacetate. The only compound obtained from the interaction of diethylamine and ethyl diazoacetate was diethylammonium 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylate; the water necessary for the hydrolysis of the ester was probably derived from the air.

In their chemical behaviour, the substituted amides resemble most closely the unsubstituted simple amides of 1:2-dihydro- and 3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylic acid (compare Curtius, Darapsky, and Müller, Abstr., 1906, i, 939; 1907, i, 359).

The methylammonium salt of 3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylmethylamide,



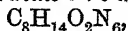
crystallises in rosettes of lemon-yellow needles, m. p. 115° (decomp.). All attempts to obtain the alkylamide by treating the salt with acids were unsuccessful. The salt is converted by acetic acid and potassium nitrite into 1:2:4:5-tetrazine-3:6-dicarboxylmethylamide,



which crystallises in slender, carmine-red leaflets, m. p. 237°, and is reduced by hydrogen sulphide to 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylmethylamide,  $\text{NHMe} \cdot \text{CO} \cdot \text{C} \begin{array}{c} \text{N} - \text{N} \\ \text{NH} \cdot \text{NH} \end{array} \text{C} \cdot \text{CO} \cdot \text{NHMe}$ , which crystallises in slender, reddish-yellow prisms, sinters at 270°, m. p. 295° (decomp.).

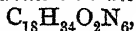
The ethylammonium salt of 3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylethylamide,  $\text{C}_{10}\text{H}_{21}\text{O}_2\text{N}_7$ , crystallises in stout, lemon-yellow rhombohedra, m. p. 105–106° (decomp.). When hydrolysed by dilute sulphuric acid, it yields ethylamine, glyoxylic acid, nitrogen (1 mol.), and hydrazine (1 mol.); glyoxylethylamide (2 mols.) is formed immediately, and was isolated and estimated as the phenylhydrazone,  $\text{C}_{10}\text{H}_{18}\text{ON}_3$ , which crystallises in almost colourless, slender, felted needles, m. p. 199–200°. 1:2:4:5-Tetrazine-3:6-dicarboxylethylamide,  $\text{C}_8\text{H}_{12}\text{O}_2\text{N}_6$ , crystallises in carmine-red leaflets, m. p. 195–196°.

1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylethylamide,



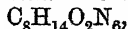
forms slender, pale yellow needles, which turn brown at 230° and decompose at 287°; it is hydrolysed by concentrated hydrochloric acid into oxalic acid (2 mols.), ethylamine (2 mols.), and hydrazine (2 mols.).

1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylethylamide,



crystallises in pale yellow, rectangular, slender leaflets, m. p. 240°.

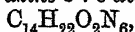
1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxyldimethylamide,



forms large, yellow, hexagonal prisms, m. p. 178–179°.

Diethylammonium 1:2-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylate,  $\text{C}_{12}\text{H}_{26}\text{O}_4\text{N}_6$ , crystallises in large, orange-yellow, hexagonal prisms, m. p. 179–180°.

1:2-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylpiperidide,



forms small, faintly yellow needles, m. p. 266° (decomp.), and is

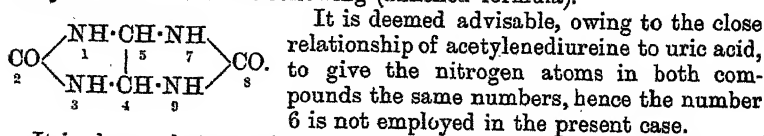
oxidised by nitric acid (D 133) to 1:2:4:5-tetrazine-3:6-dicarboxyl-piperidine,  $C_{14}H_{20}O_2N_6$ , slender, vermilion leaflets, m. p. 196° (decomp.).  
W. H. G.

$\psi$ -Diazoacetamide (3:4-Dihydro-1:2:4:5-tetrazine-3:6-dicarboxylamide). THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1909, 42, 3284—3292).—The action of diazomethane on  $\psi$ -diazoacetamide leads to the formation of a methyl derivative which must be 4-methyl-3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylamide,  $NH_2 \cdot CO \cdot C \begin{smallmatrix} \nearrow N \cdot NMe \\ \searrow N = N \end{smallmatrix} CH \cdot CO \cdot NH_2$ , since it yields nitrogen, glyoxylamide, and methylhydrazine when boiled with dilute acids. It is thus shown that the metal of the salts of  $\psi$ -diazoacetamide is undoubtedly attached to nitrogen as assumed originally (*Abstr.*, 1906, i, 939), and not to carbon as stated more recently (*Abstr.*, 1908, i, 924).

4-Methyl-3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylamide, as obtained in the manner described, is a fiery, yellow powder, m. p. 118° (decomp.), which contains as impurity, however, small quantities of 3:4-dihydro-1:2:4:5-tetrazine-3(or 6)-carboxylmethylamide-6(or 3)-carboxylamide, since, when boiled with water, it yields a solution which deposits 1:2-dihydro-1:2:4:5-tetrazine-3(or 6)-carboxylmethylamide-6(or 3)-carboxylamide,  $C_6H_8O_2N_6$ , as small, rectangular leaflets, m. p. 234° (decomp.). 4-Methyl-3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylamide, when treated with cold concentrated hydrochloric acid, yields oxamic acid hydrazide in addition to the normal products of hydrolysis; this compound probably results from the hydrolysis of the methyltetrahydrotetrazinedicarboxylamide produced by the reducing action of the glyoxylic acid, formed primarily, on the parent substance.

4-Ethyl-3:4-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylamide,  
 $C_6H_{10}O_2N_6$ ,  
is a sulphur-yellow powder, m. p. 125° (decomp.). W. H. G.

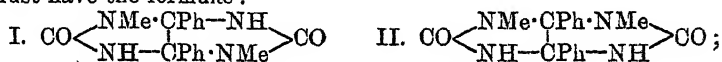
Methyl Derivatives of Diphenylacetylenediureine. HEINRICH BILTZ [with CHAIM RIMPEL] (*Annalen*, 1909, 368, 243—261. Compare *Abstr.*, 1908, i, 62).—The system of numbering employed by the author in indicating the positions of substituents in derivatives of acetylenediureine is the following (annexed formula).



It is shown that acetylenediureine has the symmetrical constitution represented by the formula just given, since methyl derivatives of 4:5-diphenylacetylenediureine containing a different number of methyl groups in the two glyoxalone rings may be prepared either by the interaction of a methylglyoxalone with a carbamide containing fewer methyl groups, or of a methylcarbamide with a glyoxalone containing a smaller number of methyl groups. For example, the 1:3-dimethyl-derivative may be prepared from 4:5-diphenyl-1:3-dimethylglyoxalone

and carbamide or from 4 : 5-dihydroxy-4 : 5-diphenyldihydroglyoxalone and *s*-dimethylcarbamide.

Although acetylenediureine yields a tetra-acetyl derivative, only a diacetyl derivative of the 4 : 5-diphenyl compound can be prepared. In order to account for this, the suggestion was made previously (*loc. cit.*) that the entrance of the acetyl groups produced a displacement of the phenyl groups which prevented the acetylation of the two remaining imino-groups. The behaviour of the methyl derivatives of diphenylacetylenediureine on acetylation gives support to this view. The fact that diphenylmethylacetylenediureine yields a diacetyl derivative shows that the displacement of the phenyl group produced by the methyl group is not sufficient to prevent acetylation of the neighbouring imino-group. It has been found possible to determine the constitutions of the two isomerides resulting from the condensation of 4 : 5-diphenyl-1-methylglyoxalone with methylcarbamide by investigating their behaviour on acetylation. The two isomerides must have the formulæ :



a compound having the first formula should yield a diacetyl derivative, whilst a substance having the second formula would only yield a mono-acetyl derivative. In agreement with this, it is found that one isomeride yields a diacetyl derivative, whilst the other yields a mono-acetyl derivative.

The methyl derivatives of 4 : 5-diphenylacetylenediureine are prepared : (1) by the condensation of 4 : 5-dihydroxy-4 : 5-diphenyldihydroglyoxalones or their ethers with carbamides in alcohol containing hydrogen chloride ; if possible, the methyl groups should be present in the glyoxalone ; (2) by treating an alcoholic solution of the diphenylglyoxalone and carbamide with bromine.

All attempts to prepare the tetramethyl derivative of 4 : 5-diphenylacetylenediureine have been unsuccessful, as were also attempts to obtain asymmetrical double ring systems by condensing 4 : 5-dihydroxy-4 : 5-diphenyldihydroglyoxalone with *o*-phenylenediamine or tolylene-3 : 4-diamine.

4 : 5-Diphenyl-1-methylacetylenediureine,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_4$ , forms colourless, glistening crystals, m. p.  $340^\circ$  (decomp.) ; the diacetyl derivative,  $\text{C}_{21}\text{H}_{20}\text{O}_4\text{N}_4$ , crystallises in flat prisms, sinters at  $230^\circ$ , m. p.  $240^\circ$  (decomp.).

4 : 5-Diphenyl-1 : 3-dimethylacetylenediureine,  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_4$ , crystallises in rhombic leaflets, or short prisms with rhombic facets, and remains unchanged at  $365^\circ$  ; the diacetyl derivative,  $\text{C}_{22}\text{H}_{22}\text{O}_4\text{N}_4$ , crystallises in large, rhombic leaflets, m. p.  $225^\circ$ . The isomeric 1 : 9-dimethyl compound forms small rhombohedra which do not melt at  $365^\circ$  ; its diacetyl derivative crystallises in rhombic leaflets, m. p.  $230^\circ$ . The isomeric 1 : 7-dimethyl compound forms large, glistening, rhombic plates, m. p.  $345^\circ$  (decomp.) ; its crystalline acetyl derivative,  $\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_4$ , has m. p.  $272-273^\circ$  (slight decomp.).

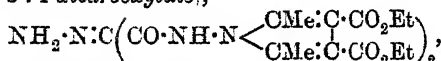
4 : 5-Diphenyl-1 : 3 : 7-trimethylacetylenediureine,  $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_4$ , crystallises in small, rectangular leaflets ; the crystalline acetyl derivative,  $\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_4$ , has m. p.  $234^\circ$ .

W. H. G.

Ethyl Mesoxalylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate). CARL BÜLOW [With OTTO SCHÄRER] (*Ber.*, 1909, 42, 3311—3326. Compare Bülow and Weidlich, *Abstr.*, 1906, i, 981; 1907, i, 1089).—A number of substances of the general formula  $\text{NHR}'\cdot\text{N}\cdot\text{C}(\text{CO}\cdot\text{NH}\cdot\text{N} < \begin{smallmatrix} \text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{R} \\ \text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{R} \end{smallmatrix})_2$  have been prepared by coupling the malonyl derivatives of Bülow and Weidlich (*Abstr.*, 1906, i, 981) with aromatic diazonium salts in the presence of sodium acetate. The phenylhydrazone derivative may also be prepared by warming ethyl mesoxalylloxime-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate) with phenylhydrazine. The oximino-compound, just mentioned, is formed when ethyl malonyl-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate) in acetic acid solution is treated with sodium nitrite.

It is found that substances having the general formula given above behave as monobasic acids, possibly because the imino-hydrogen atom of the hydrazone residue, under the influence of an alkali, wanders to one of the carbonyl groups.

Ethyl mesoxalylloxime-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate),  $\text{OH}\cdot\text{N}\cdot\text{C}(\text{CO}\cdot\text{NH}\cdot\text{N} < \begin{smallmatrix} \text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{Et} \\ \text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{Et} \end{smallmatrix})_2$ , forms white crystals, m. p. 171°, and, when heated with a 60% solution of hydrazine hydrate on a water-bath, yields ethyl mesoxalylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate),



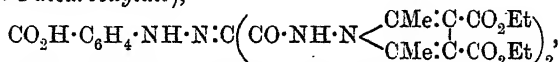
which crystallises in white needles, m. p. 204—205°.

Ethyl mesoxalylphenylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate),  $\text{C}_{23}\text{H}_{40}\text{O}_{10}\text{N}_6$ , crystallises in yellow needles, m. p. 269°, and, when boiled with aqueous sodium hydroxide and treated subsequently with acid, yields the corresponding tetracarboxylic acid,  $\text{C}_{25}\text{H}_{24}\text{O}_{16}\text{N}_6$ , a crystalline substance, m. p. 209° (decomp.). The ester is converted (1) by acetic acid and zinc dust into aniline and ethyl aminomalonyl-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate),

$\text{C}_{27}\text{H}_{37}\text{O}_{10}\text{N}_5$ , slender, white needles, m. p. 219°; (2) by the nitrogen oxides evolved from nitric acid and arsenious oxide into ethyl nitrosomesoxalyl-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate),  $\text{C}_{33}\text{H}_{39}\text{O}_{11}\text{N}_7$ , a yellow, crystalline substance, m. p. 246°.

Ethyl mesoxalyl-o-tolylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate),  $\text{C}_{34}\text{H}_{42}\text{O}_{10}\text{N}_6$ , has m. p. 248°; the corresponding m-xyllylhydrazone compound,  $\text{C}_{35}\text{H}_{44}\text{O}_{10}\text{N}_6$ , has m. p. 216°; the p-acetylaminophenylhydrazone compound,  $\text{C}_{35}\text{H}_{43}\text{O}_{11}\text{N}_7$ , commences to soften at 186°, becomes again solid at a higher temperature, and then has m. p. 225°; the  $\alpha$ -naphthylhydrazone compound,  $\text{C}_{37}\text{H}_{42}\text{O}_{10}\text{N}_6$ , crystallises in slender, brownish-yellow needles, m. p. 272°; the isomeric  $\beta$ -naphthylhydrazone compound forms very slender, yellow needles, m. p. 223°; the p-sulphophenylhydrazone compound,  $\text{C}_{33}\text{H}_{40}\text{O}_{13}\text{N}_6\text{S}$ , has m. p. 222—223°; the p-sulpho- $\alpha$ -naphthylhydrazone compound,  $\text{C}_{37}\text{H}_{42}\text{O}_{13}\text{N}_6\text{S}$ , crystallises in small, brown needles.

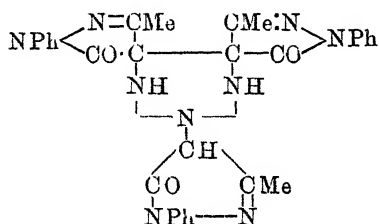
*Ethyl mesoxalyl-o-carboxyphenylhydrazone-bis-(1-amino-2:5-dimethylpyrrole-3:4-dicarboxylate)*,



has m. p. 265—266°; the corresponding *meta*-isomeride forms slender, yellow needles, m. p. 234—235°; the *para*-isomeride has m. p. 286°.

W. H. G.

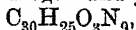
**Condensation of Phenylazoimide with Phenylmethylpyrazolone.** A. HEIDUSCHKA and O. ROTHACKER (*J. pr. Chem.*, 1909, [ii], 80, 289—302).—The red product, m. p. 184°, obtained by Walther and Rothacker by the interaction of sodium ethoxide, 1-phenyl-3-methyl-5-pyrazolone, and phenylazoimide in alcoholic solution (*Abstr.*, 1906, i, 911), has been further examined. The



annexed probable constitution is based on the analytical data and the following chemical behaviour of the substance.

The molecular weight lies between 556 and 575, and is determined by means of the salts, of which the dark red *sodium*, orange *di-sodium*, dark red *potassium*, orange *di-potassium*, dark red *ammonium*, orange

*di-ammonium*, yellow *calcium*, and orange-red *barium* salts are described. The substance contains two imino-groups and forms a red *methyl derivative*, m. p. 207°, yellow *dimethyl derivative*, m. p. 273° (decomp.), orange *diacetyl compound*, m. p. 157°, red *benzoyl derivative*, m. p. 162°, and orange-yellow *dilenzoyl derivative*, m. p. 201—202°. The substance is reduced by zinc dust, yielding rubazonic acid, and by stannous chloride and hydrochloric acid, forming the stannichloride of 4-amino-1-phenyl-3-methyl-5-pyrazolone hydrochloride. When oxidised by 20% nitric acid at 50°, the substance loses 2 atoms of hydrogen and yields a compound,



m. p. 181°, which forms brown crystals, no longer contains hydrogen replaceable by metals or alkyl groups, and is converted by dilute potassium hydroxide into pyrazole blue and bisphenylmethylpyrazolone almost exactly in the ratio 1 : 2.

A chloroform solution of the red product is converted by bromine into an unstable dibromo-*derivative*,  $\text{C}_{30}\text{H}_{25}\text{O}_3\text{N}_9\text{Br}_2$ , and by chlorine into 4:4-dichloro-1-phenyl-3-methyl-5-pyrazolone.

C. S.

**Reductions with Ethyl Alcohol.** GIACOMO PONZIO (*Gazzetta*, 1909, 39, ii, 321—324).—Acylazoaryl derivatives (this vol., i, 681) are readily reduced to the corresponding acylarylhidrazines by boiling their absolute alcoholic solutions until these become colourless (compare Paternò, this vol., i, 240). This reaction, which is accompanied by the formation of acetaldehyde, is possibly applicable to other azo-compounds, but it seems probable that the simultaneous action of either light or a high pressure would be necessary. When

reduced in this way, benzoylazobenzene yields  $\alpha$ -benzoyl- $\beta$ -phenylhydrazine; *p*-toluoylazobenzene,  $\alpha$ -*p*-toluoyl- $\beta$ -phenylhydrazine; anisoylazobenzene,  $\alpha$ -anisoyl- $\beta$ -phenylhydrazine; benzoylazo-*p*-bromobenzene,  $\alpha$ -benzoyl- $\beta$ -*p*-bromophenylhydrazine; *p*-toluoylazo-*p*-bromobenzene,  $\alpha$ -*p*-toluoyl- $\beta$ -*p*-bromophenylhydrazine; anisoylazo-*p*-bromobenzene,  $\alpha$ -anisoyl- $\beta$ -*p*-bromophenylhydrazine; benzoylazo-*p*-chlorobenzene,  $\alpha$ -benzoyl- $\beta$ -*p*-chlorophenylhydrazine; and benzoylazo-*o*:*p*-dichlorobenzene,  $\alpha$ -benzoyl- $\beta$ -*o*:*p*-dichlorophenylhydrazine. T. H. P.

[Sulphonation of 2':3-Dichloro-4-aminoazobenzene.] AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 210598).—2':3-Dichloro-4-aminoazobenzene disulphonic acid is prepared by sulphonating 2':3-dichloro-4-aminoazobenzene (Niemętowski, Abstr., 1903, i, 133). The dye is a yellowish-brown powder. F. M. G. M.

Action of Potassium Hydroxide on Aniline. A. BACOVESCU (*Ber.*, 1909, 42, 2938—2940).—Wohl (Abstr., 1900, i, 157) showed that on heating nitrobenzene with potassium hydroxide, potassium-*o*-nitrophenol is formed; subsequently Wohl and Aue (Abstr., 1901, i, 612) isolated azoxybenzene as the chief product of the action of potassium hydroxide on a mixture of aniline and nitrobenzene. It is now shown that by the action of potassium hydroxide in large excess on aniline, azobenzene and the *o*-benzeneazophenol first described by Bamberger (Abstr., 1900, i, 531) are formed. Potassium hydroxide forms benzeneazophenol from azobenzene, and converts hydrazobenzene into azobenzene. E. F. A.

Behaviour of Ethers of *o*-Hydroxyazo-compounds when Reduced with Stannous Chloride and Hydrochloric Acid. PAUL JACOBSON (*Annalen*, 1909, 369, 1—40. Compare Jacobson, Franz, and Zaar, Abstr., 1904, i, 121; Jacobson and Hönigsberger, *ibid.*, 202).—The present communication deals with the reduction in acid solution of azophenol ethers containing the grouping  $\text{C}_6\text{H}_4\text{N}(\text{N}^\cdot\text{Et})_2$  (2) and a methyl group in the position para to the azo-group.

In all the cases investigated it is found that, apart from the bases formed by the fission of the azo-compound, considerable quantities of two bases, namely, a parasemidine and a diphenyl base, are formed. For example, *p*-tolueneazo-*o*-phenetole yields 4-amino-3'-ethoxy-4-methyldiphenylamine and 4':6-diamino-3'-ethoxy-3-methyldiphenyl. Occasionally, very small quantities of an orthosemidine are also formed, but, as found formerly (*loc. cit.*), the presence of a substituent ortho to the azo-group hinders the orthosemidine transformation.

[With L. HUBER].—*p*-Tolueneazo-*o*-phenetole,  $\text{C}_{15}\text{H}_{16}\text{ON}_2$ , prepared by condensing *p*-nitrosotoluene with *o*-phenetidine in glacial acetic acid, crystallises in long, red needles and prisms, m. p. 92—93°.

4'-Amino-3'-ethoxy-4-methyldiphenylamine,  $\text{C}_{15}\text{H}_{18}\text{ON}_2$ , crystallises in small, colourless rods, m. p. 75°; the hydrochloride,  $\text{C}_{15}\text{H}_{18}\text{ON}_2\text{HCl}$ , forms slender, white needles; the salicylidene derivative,  $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2$ , crystallises in microscopic, yellow plates with a violet-red shimmer, m. p. 133—134°; the acetyl derivative,  $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2$ , forms fan-like

aggregates of small, slender, bluish-white needles, m. p. 168—169°. The base is oxidised by chromic acid, yielding 2-ethoxy-*p*-benzoquinone-*p*-tolylimine,  $C_9H_4Me \cdot N : C_6H_3(OEt) : O$ , which forms large, red crystals, m. p. 137—138°.

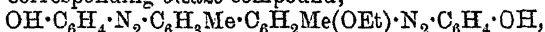
4':6'-Diamino-3'-ethoxy-3-methyldiphenyl,  $C_{15}H_{18}ON_2$ , crystallises in tufts of slightly yellow needles, m. p. 88—89°; the *di-p*-nitrobenzylidene derivative,  $C_{29}H_{24}O_5N_4$ , forms long, yellowish-red needles, m. p. 204—205°; the *dibenzoyl* derivative,  $C_{29}H_{26}O_5N_2$ , crystallises in white, microscopic rods, m. p. 174°.

The reduction of *p*-tolueneazo-*o*-phenetole with stannous chloride and hydrochloric acid yields, in addition to the bases just described, small quantities of (1) a substance,  $C_{15}H_{17}O_2N$ , probably 6-amino-4'-hydroxy-5'-ethoxy-3-methyldiphenyl, which forms small, bluish-white crystals, m. p. 139—140°; (2) 6-amino-2'-ethoxy-3-methyldiphenylamine,  $NH_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4 \cdot OEt$ , which forms small, white crystals, m. p. 75—77°, and condenses with benzil, yielding the *stilbazonium* base,  $CPh(OH) \cdot N \cdot C_6H_4 \cdot OEt$ ,  $CPh \cdot N - C_6H_3Me$ , obtained in small, pale yellow, hexagonal plates, m. p. 140—142°.

[With E. JANKOWSKI.]—The reduction of *p*-tolueneazo-*p*-cresetole has already been investigated by Jacobson and Piepenbrink (compare Abstr., 1895, i, 26). The results recorded by these authors have been confirmed and their work extended.

4-Ethoxy-2:5-toluquinone,  $C_9H_{10}O_3$ , prepared by the oxidation of 4-amino-5-ethoxy-2:4'-dimethyldiphenylamine with chromic acid, crystallises in yellow cubes, m. p. 101°, and when reduced with sulphurous acid yields 2:5-dihydroxy-4-ethoxytoluene,  $C_9H_{12}O_3$ , colourless plates, m. p. 131°.

4:6'-Diamino-5-ethoxy-2:3'-dimethyldiphenyl could not be obtained in a crystalline form; when diazotised and coupled with phenol it yields the corresponding *bisazo*-compound,



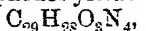
a brown, amorphous powder, m. p. 135°.

[With H. L. FULDA.]—*p*-Tolueneazo-4-*m*-xylenol (6-hydroxy-3:5:4'-trimethylazobenzene),  $C_{15}H_{16}ON_2$ , prepared by coupling *p*-toluene-diazonium chloride with 4-*m*-xylenol, crystallises in bright red needles, m. p. 99°; the *ethyl* ether,  $C_{17}H_{20}ON_2$ , forms red, prismatic leaflets, m. p. 51·5—52·5°, and yields on reduction *p*-toluidine, 4-ethoxy-5-m-xylidine, 4-amino-3-ethoxy-2:6:4'-trimethyldiphenylamine, small quantities of the corresponding orthosemidine, and 4:6'-diamino-3-ethoxy-2:6:3'-trimethyldiphenyl.

The *acetyl* derivative of 4-ethoxy-5-*m*-xylidine,  $C_{12}H_{17}O_2N$ , has m. p. 65—66°; the *thiocarbamide*,  $CS(NH \cdot C_6H_3Me_2 \cdot OEt)_3$ , crystallises in long, white prisms, m. p. 141—142°.

4-Amino-3-ethoxy-2:6:4'-trimethyldiphenylamine is a colourless oil; the *salicylidene* derivative,  $C_{24}H_{26}O_3N_2$ , crystallises in yellow needles, m. p. 147—148°. The base is oxidised by chromic acid, yielding 4-ethoxy-*m*-2:5-xyloquinone,  $C_{10}H_{12}O_3$ , which crystallises in long, brownish-yellow needles, m. p. 41—42°, and is reduced by sulphurous acid to the corresponding *dihydroxy*-compound crystallising in long, colourless needles.

4 : 6'-Diamino-3-ethoxy-2 : 6 : 3'-trimethyldiphenyl,  $C_{11}H_{22}ON_2$ , crystallises in glistening, transparent, colourless rhombohedra, m. p. 117—118°; the *disalicylidene* derivative,  $C_{31}H_{20}O_8N_2$ , forms oblique-angled plates, m. p. 201—202°; the *diformyl* derivative,  $C_{19}H_{22}O_8N_2$ , crystallises in small, colourless prisms, m. p. 189°. The base when diazotised and coupled with phenol yields the *bisazo*-compound,



a dark brown powder decomposing at 145°.

[With O. FABIAN.]—4-m-Xyleneazo-*p*-cresol (6-hydroxy-3 : 2' : 4'-trimethylazobenzene),  $C_{15}H_{16}ON_2$ , prepared from 4-m-xyldine and *p*-cresol, crystallises in reddish-brown needles, m. p. 85°, b. p. 230—233°/30 mm. (very slight decomp.); the *ethyl ether*,  $C_{17}H_{20}ON_2$ , forms red, oblique-angled plates, m. p. 51°, b. p. 238—242°/25 mm., and when reduced yields 4'-amino-5'-ethoxy-2 : 4 : 2'-trimethyldiphenylamine and 4 : 2'-diamino-5-ethoxy-2 : 3' : 5'-trimethyldiphenyl. The former base could not be crystallised; the *acetyl* derivative,  $C_{19}H_{24}O_2N_2$ , forms tufts of white, hair-like needles, m. p. 114°; the *salicylidene* derivative,  $C_{34}H_{26}O_2N_2$ , crystallises in long, slender, orange needles, m. p. 116°. The base is oxidised by chromic acid, yielding 4-ethoxy-2 : 5-toluquinone-2(4)-m-xylylimine,  $CMe \begin{smallmatrix} \text{CH:CMe} \\ \text{CH-CH} \end{smallmatrix} > C \cdot N : C < \begin{smallmatrix} CMe=CH \\ CH:C(OEt) \end{smallmatrix} > C : O$ , which crystallises in garnet-red prisms, m. p. 118°, and is reduced by zinc dust and acetic acid to 4'-hydroxy-5'-ethoxy-2 : 4 : 2'-trimethyldiphenylamine,  $C_{17}H_{21}O_2N$ , white, elongated, hexagonal plates, m. p. 103°.

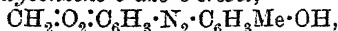
4 : 2'-Diamino-5-ethoxy-2 : 3' : 5'-trimethyldiphenyl, b. p. 240—260°/50 mm., forms a *disalicylidene* derivative,  $C_{31}H_{20}O_8N_2$ , crystallising in nodules, m. p. 161—162°, and when boiled with glacial acetic acid yields a basic substance crystallising in pyramids, m. p. 167—168°.

W. H. G.

Hydroxyazo-derivatives obtained from 4-Amino-1 : 2-catechol Methylene Ether [4-Amino-1 : 2-methylenedioxybenzene]. EFISIO MANELI (*Gazzetta*, 1909, 39, ii, 314—321).—The author has prepared several azo-phenolic derivatives from 4-amino-1 : 2-methylenedioxybenzene (compare this vol., i, 711). These compounds give coloured crystals and act as acid colouring matters, dyeing wool, silk, and cotton in acid solutions.

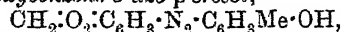
1 : 2-Methylenedioxybenzeneazophenol,  $CH_2 : O_2 : C_6H_3 \cdot N_2 \cdot C_6H_4 \cdot OH$ , forms yellow crystals, m. p. 180° (decomp.), and yields *p*-aminophenol when reduced by means of phenylhydrazine.

1 : 2-Methylenedioxybenzene-6-azo-*o*-cresol,



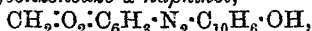
prepared from *o*-cresol, crystallises in yellow scales, m. p. 157°.

1 : 2-Methylenedioxybenzene-5-azo-*p*-cresol,



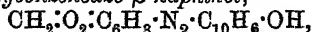
prepared from *p*-cresol, has m. p. 165°.

1 : 2-Methylenedioxybenzeneazo- $\alpha$ -naphthol,



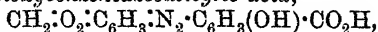
forms dark red crystals, m. p. 170° (decomp.).

1 : 2-Methylenedioxybenzeneazo- $\beta$ -naphthol,



forms red scales, m. p. 156—158°, and yields an *acetyl* derivative,  $C_{19}H_{14}O_4N_2$ , m. p. 105—107°.

1:2-Methylenedioxybenzeneazosalicyclic acid,



forms yellow crystals, m. p. 218—222°.

T. H. P.

**Thiophenols. I. *o*-Azothioanisole and *o*-Thiodianisidine.** KURT BRAND (*Ber.*, 1909, 42, 3463—3468).—The sodium derivatives of the nitrophenyl mercaptans necessary for the formation of the thioethers are obtained best by reducing the dinitrodiphenyl disulphides in the presence of sodium hydroxide by sodium hydrosulphide, sodium sulphide, or sodium disulphide. When too much reducing agent is used, the nitro-group is also attacked.

A solution of sodium *o*-nitrophenyl mercaptide, obtained by heating an alcoholic suspension of 1:1'-dinitrophenyl disulphide with aqueous sodium hydroxide (2 mols.) and sodium hydrosulphide ( $> \frac{1}{2}$  mol.), or sodium sulphide ( $\frac{1}{2}$  mol.), or sodium disulphide ( $\frac{1}{3}$  mol.), yields *o*-nitrothioanisole by treatment with aqueous potassium methyl sulphate (2 mols.) or with sodium hydroxide and methyl sulphate. *o*-Nitrothioanisole,  $NO_2 \cdot C_6H_4 \cdot SMe$ , m. p. 85—87°, crystallises in yellow needles, and is reduced by Elbs's electrolytic method to *o*-azothioanisole,  $SMe \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot SMe$ , m. p. 156—158°, which forms an intensely blue, crystalline hydrochloride. *o*-Hydrazothioanisole,  $C_8H_{16}N_2S_2$ , m. p. 104°, is obtained by reducing *o*-azothioanisole, suspended in ethyl acetate and alcohol, by a solution of sodium or ammonium hydrosulphide, or more conveniently by reducing alcoholic *o*-nitrothioanisole by zinc dust and sodium hydroxide. It crystallises in colourless needles, is oxidised in alcoholic solution by air or mercuric oxide to *o*-azothioanisole, and is converted by 30% hydrochloric acid into the *hydrochloride* of *o*-thiodianisidine,  $C_{14}H_{16}N_2S_2 \cdot 2HCl$ , m. p. 260° (decomp.). The free base,  $C_{14}H_{16}N_2S_2$ , m. p. 110—112°, liberated by ammonium hydroxide, forms a *diacetyl* derivative, m. p. 245—247°, and a bisdiazo-compound which unites with phenols and amines to form substantive cotton dyes.

C. S.

**Diazotisation of Feebly Basic, Sparingly Soluble Primary Amines.** OTTO N. WITT (*Ber.*, 1909, 42, 2953—2961).—Primary amines of pronounced basic character are very easily diazotised in acid aqueous solution by means of the theoretical quantity of sodium nitrite. When, however, acid groups are introduced into the benzene nucleus, the salts of such amines are more readily dissociated, and it becomes increasingly difficult to diazotise them. It has been found that strong nitric acid ( $D = 1.48$  and higher) forms an excellent solvent for such amines and also for nitrous acid. Both the latter and also nitrosylsulphate act as very efficient diazotising agents in presence of nitric acid. No side reactions take place, even if the acid is warmed to 60° or 70°. This is due to the very rapid formation of the diazonium nitrate, which itself is totally resistant towards nitric acid. Diazotisation in nitric acid solution is most conveniently effected by adding exactly the amount of sulphurous acid required to reduce sufficient

nitric to nitrous acid. Equally convenient is the use of the commercial potassium metadisulphite,  $K_2S_2O_5$ , which dissolves in nitric acid, forming nitrous acid and potassium pyrosulphate. The base to be diazotised is finely powdered with the metadisulphite, and the mixture introduced in small portions into the nitric acid.

These diazo-compounds can be preserved in the nitric acid solution for months without decomposition.

When dichloronitroaniline is oxidised with strong nitric acid, *dichloro-p-nitrophenylnitroamine* is formed; this separates in colourless crystals, m. p.  $120^\circ$ . It has acid properties, turns litmus red, and forms crystalline salts with bases. It probably has the constitution of a  $\psi$ -acid in the free state. The metallic salts are easily soluble with the exception of the *thorium* salt; insoluble salts are formed with diazonium bases.

E. F. A.

**Inhibiting Action of Neutral Salts on the Swelling of Fibrin through Acids and Alkalis.** MARTIN H. FISHER and GERTRUDE MOORE (*Zeitsch. Chem. Ind. Kolloide*, 1909, 5, 197—199. Compare Abstr., 1908, i, 929).—Neutral salts hinder the action of alkalis and acids in producing swelling of fibrin. Quantitative investigation of a number of salts leads to the conclusion that the ions can each be given an inhibition value.

The inhibiting effect brought about by adding comparable amounts of equimolecular salt solutions under identical conditions is proportionate to the sum of the values for the two ions in question in each case. Tables of quantitative determinations are given. Irregular results are to be expected, and are found, when the acid or alkali bringing about the swelling and the neutral salt interact chemically.

G. S. W.

**Hydrolysis of Casein and the Detection of the Monoamino-acids Formed.** R. ENGLAND (*Ber.*, 1909, 42, 2962—2969).—Most of the monoamino-acids as obtained by the hydrolysis of proteins, being amphoteric indifferent substances, are difficult to isolate. The amino-acids are converted by alkyl halides into betaines, which form characteristic aurichlorides, by means of which they can be identified even when present in small quantity. Use may be made of the varying solubility of their double salts with mercury, platinum and gold chlorides to separate the various amino-acid betaines.

The method is applied to the isolation of the products of hydrolysis of casein.

The methylation must be carried out in the cold; at higher temperatures a number of high molecular and, in part, oxygen-free condensation products are formed, all of which are characterised by the pronounced tendency to crystallise of their sparingly soluble auri- and platini-chlorides. In view of the well known tendency of the animal and vegetable organisms to bring about methylation, it is possible that similar products may be formed in the living organism. An explanation is also afforded of the wide distribution of betaine in plants as well as of its higher homologues. The diamino-acids and the proteins themselves are less easily methylated.

E. F. A.

**The Action of Light on Blood-pigments and Blood-corpuscles, and the Optical Sensitisation of the Action.** K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1909, 19, 435—493).—A Kromayer mercury lamp was used as the source of light, and the blood or other liquid was exposed in specially devised vessels which could be shaken so as to continually expose fresh surfaces. The sides of the vessels exposed to light could be either of quartz or glass, which permit the passage of different light rays. The vessels could be evacuated, so that the light action could be studied in a vacuum or analyses made of the gases from time to time. It was found that the original blood-pigment is converted by light into methæmoglobin, which further changes into hæmatin. This action only takes place in the presence of oxygen. Reduced hæmoglobin is not changed by light. The action is due chiefly to rays of wave-length under  $310\mu$ , although those of greater length are not entirely inactive. The change by light of hæmoglobin into methæmoglobin follows the course of a unimolecular reaction. Methæmoglobin is converted in a vacuum by light into reduced hæmoglobin. If the mixture is placed in the dark, the oxygen thus set free leads to the formation of oxyhæmoglobin. Hæmatin in the light is changed into hæmochromogen; the reaction can be reversed by keeping the mixture thus obtained in the dark. Carbon monoxide-hæmoglobin is partly changed by light into reduced hæmoglobin; this action is also reversible on darkening. Blood-corpuscles are lysed by light, both in presence of air and in a vacuum, chiefly by rays of smaller wave-length than  $310\mu$ . Colour sensitisers increase the reaction rate of light actions only in such reactions accompanied by a scission of oxygen. The sensitiser acts as a light absorbing, readily oxidisable substance.

S. B. S.

**The Behaviour of Acetylene to Blood.** LOUIS LEWIN, A. MIETHE, and E. STENGER (*Pflüger's Archiv*, 1909, 129, 603—606).—After treatment of blood with acetylene, the pigment is apparently unaltered; chemically and spectroscopically it behaves like normal blood.

W. D. H.

**The Pigment of Blood. II. So-called Hæmatopyrrolidinic Acid.** OSCAR PILOTY and S. MERZBACHER (*Ber.*, 1909, 42, 3253—3258).—The oil obtained by the oxidation of hæmatopyrrolidinic acid (compare this vol., i, 539) is named provisionally *hæmopyrroline*. It is also formed together with hæmopyrrolecarboxylic acid by fusing the zinc salt of hæmatopyrrolidinic acid with potassium hydroxide at  $270-320^\circ$ , and apparently consists of a mixture of three compounds, namely: (1) an oil,  $C_8H_{15}N$  or  $C_8H_{12}N$ , probably a hydrogenated hæmopyrrole, the crystalline *picrate*,  $C_{14}H_{18}O_7N_4$  or  $C_{14}H_{16}O_7N_4$ , of which has m. p.  $99-100^\circ$ ; (2) an oil,  $C_7H_{11}N$  (?), probably a lower homologue of hæmopyrrole; (3) an oil with a high b. p., having a piperidine-like odour, which is possibly a pyrogenous product and may be regarded as an impurity.

It has been shown previously (*loc. cit.*) that the hæmopyrrole and hæmopyrrolecarboxylic acid complexes are present as such in hæmatopor-

phyrin; since hæmatopyrrolidinic acid also contains the hæmopyrrole-carboxylic acid complex, it follows that hæmatoporphyrin contains two carboxyl groups. It may be assumed, therefore, that the atom of iron in hæmin and hæmatin is combined with these two carboxyl groups and with the four nitrogen groups of the four pyrrole nuclei to form a complex.

W. H. G.

**The Pigment of Blood. III. New Cleavage of Hæmatoporphyrin.** OSCAR PILOTY and S. MERZBACHER (*Ber.*, 1909, 42, 3258—3261. Compare preceding abstract).—It is shown that hæmopyrrole and hæmopyrrolecarboxylic acid are primary products of the degradation of hæmatoporphyrin, since the latter compound when fused with potassium hydroxide yields substances which contain carbon and hydrogen in the same proportions as hæmopyrrole and hæmopyrrolecarboxylic acid.

Hæmatoporphyrin when fused with potassium hydroxide yields an oil, termed provisionally *hp-pyrrole*, which has b. p. 70—95°/35 mm., and yields on fractionation (1) an oily substance,  $C_8H_9N(?)$ , probably a lower homologue of hæmopyrrole; (2) an oily substance,  $C_8H_{13}N(?)$ , the *picrate* of which forms large, prismatic leaflets, m. p. 126°. An acid is also formed simultaneously, which crystallises in colourless, odourless leaflets, m. p. about 100°, and is very similar to hæmopyrrole-carboxylic acid.

W. H. G.

**The Pentose in Nucleic Acids. II.** PHOEBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1909, 42, 3247—3251. Compare this vol., i, 541, 620).—The pentose derived from inosic acid, guanylic acid, and yeast nucleic acid is undoubtedly *d*-ribose, and for the following reasons: (1) It has the same m. p. and approximately the same optical rotatory power, but of the opposite sign, as *l*-ribose (compare A. van Ekenstein and Blanksma, this vol., i, 457); (2) when oxidised it yields *d*-ribotrihydroxyglutaric acid, which is obtained as its lactone (compare Fischer and Piloty, *Abstr.*, 1892, 437), and (3) the *p*-bromophenylosazone is the antipode of arabinose-*p*-bromophenylosazone.

*d*-Ribose-*p*-bromophenylosazone,  $C_{17}H_{18}O_8N_4Br_2$ , forms small, glistening, pale yellow, hexagonal plates, sinters at 175°, m. p. 180—185° (corr.),  $\alpha_D$  in a 2-dm. tube ( $c=0.1004$  gram in 5 c.c. of alcohol-pyridine, 2:3) =  $-0.56^\circ$  (10 mins. after dissolution),  $-0.36^\circ$  (final value); ( $c=0.0499$  gram in 5 c.c. of alcohol) =  $-0.12^\circ$  (10 mins. after dissolution),  $-0.08^\circ$  (final value). The *additive* compound with 1 mol. of pyridine(?) forms long, slender, matted needles, sinters at 75°, and shrinks together at 80—85°.

*l*-Arabinose-*p*-bromophenylosazone (compare Neuberg, *Abstr.*, 1900, i, 139) forms crystals having the same appearance and m. p. as its antipode; the final values of  $\alpha_D$  were  $+0.40^\circ$  ( $c=0.1$  gram in 5 c.c. of alcohol-pyridine) and  $+0.09^\circ$  ( $c=0.0501$  gram in 5 c.c. of alcohol).

W. H. G.

**The Pentose from the Pancreas.** BRUNO REWALD (*Ber.*, 1909, 42, 3134—3136).—The author's object is to settle the identity of the pentose which is extracted in the form of a protein compound when

pancreatic glands are boiled with water. The pentose is set free on hydrolysing this protein with acid, and was considered by Neuberg to be *l*-xylose. Recently, Levene has regarded it as a new pentose, carnose, or *d*-ribose (this vol., i, 447, 620). The author finds that the *p*-bromophenylosazone of the pentose, prepared from the hydrolysed pancreatic extract, is identical with *p*-bromophenyl-*l*-xylosazone. A mixture of the two substances possessed the same m. p., 204°.

R. V. S.

**The Occurrence of Azelaic Acid among the Oxidation Products of Keratin.** TH. LISSIZIN (*Zeitsch. physiol. Chem.*, 1909, 62, 226—228).—Small quantities of azelaic acid are formed when keratin is oxidised with potassium permanganate. From 240 grams of keratin, 0.0468 gram of the acid was obtained. The amount is about the same when horn which has been extracted with ether is used instead of keratin.

J. J. S.

**Comparative Investigations on the Composition and Cleavage Products of Different Kinds of Silk.** V. Mono-amino-acids from Niët ngõ tsám Silk from China. EMIL ABDERHALDEN and G. ALESSANDRO BROSSA. VI. Monoamino-acids from Indian Tussore Silk. EMIL ABDERHALDEN and WLADIMIR SPACK. VII. Monoamino-acids from the Gelatin (leim) of Canton Silk. EMIL ABDERHALDEN and WORMS (*Zeitsch. physiol. Chem.*, 1909, 62, 129—130, 131—132, 142—144. Compare this vol., i, 757).—The following table gives the percentages of monoamino-acids derived from the three sources above specified :

	Niët ngõ tsám silk.	Indian Tussore silk.	Silk gelatin of Canton silk.
Glycine .....	24.0	9.5	1.2
Alanine .....	18.5	24.0	9.2
Leucine .....	1.2	1.5	5.0
Serine .....	1.5	2.0	5.8
Aspartic acid .....	2.0	2.5	2.5
Glutamic acid .....	3.0	1.0	2.0
Phenylalanine .....	1.0	0.6	0.6
Tyrosine .....	7.8	9.2	2.3
Proline .....	1.2	1.0	2.5

W. D. H.

**The Products Obtained by the Partial Hydrolysis of Proteins.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1909, 62, 315—321. Compare this vol., i, 273).—By what is described as a lucky accident, it was found possible to prepare glycyl-8-tyrosine directly from the products of partial hydrolysis of silk. The hydrolysis had been carried out with 75% sulphuric acid at room temperature. Similarly, two dipeptides, one of them leucyl-glycine and the other probably glycyl-leucine, were obtained from elastin. Full details of the preparation, separation, and identification of the dipeptides are given.

W. D. H.

**Hydrolysis of Wild Silk.** UMETARO SUZUKI, K. YOSHIMURA, and R. INOUE (*J. Coll. Agric. Imp. Univ. Tōkyō*, 1909, 1, 59—75).—De-

terminations of nitrogen dissolved by hot hydrochloric acid, insoluble nitrogen, and ash in wild silks gave the following results :

	Dry matter.	Per cent. in dry matter.		
		Soluble N.	Insoluble N.	Ash.
1. <i>Antheraea Pernyi</i> . . .	86.84	16.39	2.48	2.92
2. „ <i>Yamamai</i> . . .	88.71	17.26	0.47	4.73
3. <i>Bombyx mori</i> . . . . .	87.10	18.86	0.12	0.63
4. <i>Caligula japonica</i> . . . .	88.29	15.77	0.96	3.85

The following amounts of the various cleavage products were found (% in dry matter) :

	1.	2.	4.		1.	2.	4.
Glycine . . . . .	5.7	6.3	7.7	Aspartic acid . . . . .	1.0	1.0	0.2
<i>d</i> -Alanine . . . . .	4.8	7.2	15.3	<i>L</i> -Tyrosine . . . . .	1.4	2.0	5.5
<i>L</i> -Leucine . . . . .	1.2	1.3	7.95	Histidine . . . . .	2.7	1.6	1.0
Phenylalanine . . . .	-	+	+	Arginine . . . . .	3.1	3.8	1.74
Proline . . . . .	+	+	* 4.0	Lysine . . . . .	?	7.4	2.45
Glutamic acid . . . .	+	0.6	0.2	Ammonia . . . . .	0.6	0.8	0.8
			?				

\* Active and racemic respectively.

N. H. J. M.

**The Non-existence of Protagon as a Definite Chemical Compound.** OTTO ROSENHEIM and M. CHRISTINE TEBB (*Quart. J. exp. Physiol.*, 1909, 2, 317—333).—A continuation of the controversy with Cramer. Fresh experimental and analytical evidence is adduced which confirms the authors' previous contention that "protagon" is not a definite chemical compound, but a mixture of various lipoids.

W. D. H.

**Electrolytic Dissociation and Physiological Activity of Pepsin and Trypsin.** JACQUES LOEB (*Biochem. Zeitsch.*, 1909, 19, 534—537).—The accelerating action of acids in the case of pepsin and of alkalis in the case of trypsin can be explained on the assumption that the former is a weak base and the latter a weak acid, and the addition of the acid or alkali causes the formation of salts. The salts of weak acids and bases are more strongly dissociated than the acids and bases themselves. If the enzyme action, therefore, is due to the enzyme ion, its acting mass will be greater in the presence of enzyme salts. These remarks also apply if the enzyme be of amphoteric character, as in this case the addition of acid or alkali will cause dissociation into either electronegative or electropositive ions as the case may be.

S. B. S.

**Action of Trypsin on 3:5-Di-iodo-*L*-tyrosine.** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, 62, 432—442. Compare this vol., i, 123).—A faintly alkaline solution of 3:5-di-iodotyrosine can be left for several weeks at 35—37° without any appreciable amount of iodine being removed, but in the presence of trypsin appreciable amounts of iodine are eliminated as hydrogen iodide. The amount varies with the specimen of pancreatin used, and in some cases is as high as 45% of the

total iodine, and the general behaviour is similar to that of iodo-thyreoglobulin.

The solutions of di-iodotyrosine which have undergone considerable decomposition do not give Millon's reaction, and it is suggested that the decomposition consists in the replacement of iodine by hydroxyl, and that the resulting  $\alpha$ -amino- $\beta$ -3:4:5-trihydroxyphenylpropionic acid is immediately oxidised.

Gorgonia corals also give up their iodine as hydriodic acid when treated with pancreatin in faintly alkaline solution (compare Drechsel, Abstr., 1896, ii, 378). J. J. S.

**Intracellular Enzymes of Lower Fungi, especially those of *Penicillium camemberti*.** ARTHUR WAYLAND DOX (*J. Biol. Chem.*, 1909, 6, 461—467).—The enzymes in *Penicillium camemberti* were those specially investigated, as a contribution to the knowledge of ripening in soft cheeses. The proteolytic enzyme closely resembles erepsin; it does not act on native proteins, except on casein, but it rapidly decomposes proteoses. Nuclease, amidases (liberating ammonia from amides), an enzyme which resolves hippuric acid into benzoic acid and glycine, emulsin, amylase, inulase, raffinase, sucrase, lactase, and maltase were also found, but the presence of lipase is doubtful. W. D. H.

**Studies on Enzymes. II. Measurement and Meaning of the Concentration of the Hydrogen Ions in Enzymatic Processes.** SÖREN P. L. SÖRENSEN (*Biochem. Zeitsch.*, 1909, 21, 131—304. Compare Abstr., 1908, i, 115).—A distinction has to be made between degree of acidity and the concentration of hydrogen ions, only the latter having a rôle in enzymatic decompositions. Methods for measuring the concentration of hydrogen ions, in which the concentration changes during the measurement (as in the usual acidimetric and alkalimetric titration methods), are useless, and the "catalytic" methods generally fail. Two methods are recommended, the accurate electro-method and the less exact, but very simple, colorimetric method.

The optimal concentration of hydrogen ions in invertin cleavage remains almost the same, independently of the kind and amount of the invertin and of the acid. Under the conditions employed, the optimal concentration was  $p_H = 4.4$  to  $4.6$ .

With invertin the optimal point of the concentration of hydrogen ions moves slightly, as the duration of the experiment increases towards the alkaline side. In catalase cleavage at  $0^\circ$  the optimal concentration is very near the neutral point, but seems to tend towards the acid side when the time is increased.

At a temperature of  $37^\circ$ , the optimal concentration in pepsin cleavage distinctly depends on the time. N. H. J. M.

**Effect of Shaking on Ptyalin.** MARIE M. HARLOW and PERCY G. STILES (*J. Biol. Chem.*, 1909, 6, 359—362).—Mere shaking in a bottle does not affect the activity of ptyalin, but reduction in digestive power occurs when the surface is increased by the introduction of glass

beads or glass wool. This is believed to be due to adsorption upon the glass. If ptyalin is shaken in the presence of starch, no loss of digestive power occurs; it is therefore suggested that the enzyme is protected by its substrate. A few experiments with taka-diasase gave similar results.

W. D. H.

**Retarding Influence of Certain Compounds on Hydrolysis of Glucosides by Emulsin.** Mlle. A. FICHTENHOLZ (*J. Pharm. Chim.*, 1909, [vi], 30, 199—204).—Attention has already been drawn to the extreme slowness with which emulsin hydrolyses arbutin (Abstr., 1908, ii, 995); this appears to be due to the retarding influence of the quinol produced during the decomposition. The addition of quinol, however, effected only a slight retardation of the hydrolysis of other glucosides, such as salicin, gentiopicrin, and amygdalin, which do not produce this substance themselves under the action of the ferment. Gallic and tannic acids exert a retarding influence on the hydrolysis of glucosides by emulsin, but the extent to which this is exhibited depends mainly on the nature of the glucoside.

W. O. W.

**Influence of Salts on the Dialysis of Peroxydase. I.** JAN BIELECKI (*Biochem. Zeitsch.*, 1909, 21, 103—107).—The addition of nitrates (of potassium, ammonia, and calcium) to a solution of peroxydase leads to its passing through a dialyser, in amounts roughly proportionate to the amount of salt added. Whether the nitrate acts as a kind of inorganic co-enzyme, or whether more complex questions still are involved, is left open.

W. D. H.

**General Process of Oxidation by Oxidising Ferments.** ÉMILE BOURQUELOT (*J. Pharm. Chim.*, 1909, [vi], 30, 101—105).—The author reviews recent work carried out by his pupils in connexion with oxidising ferments. He does not agree with the view that tyrosinase is the active substance in *Russula* extract which transforms morphine into  $\psi$ -morphine, inasmuch as gum arabic, which has no action on tyrosine, is capable of oxidising morphine. There is no evidence against the existence of two oxidising ferments, laccase and tyrosinase, and possibly a third, "morphinase," may exist (compare Bougault, Abstr., 1902, i, 638; Bertrand, this vol., i, 601).

W. O. W.

**Specific Action of Oxydases.** JULES WOLFF (*Compt. rend.*, 1909, 149, 467—469. Compare this vol., i, 279).—A record of observations, some of which have been published previously, which support BourqueLOT's views on the existence of oxidising ferments other than laccase and tyrosinase (preceding abstract). Extract of *Russula* brings about oxidation of orcinol, and the action is accelerated by the addition of sodium hydrogen phosphate to the solution; an extract containing laccase, however, is inactive except in presence of an alkali. The specific action of the *Russula* extract depends, therefore, either on the presence of a new specific diastase, *orcinase*, or on the influence of other factors, such as the alkalinity of the medium, in conjunction with the ferments already recognised.

W. O. W.

Oxidations of Biological Importance. II. The Preparation of Pure *Medicago* Laccase and its Chemical Constitution. III. HANS EULER and IVAN BOLIN (*Zeitsch. physiol. Chem.*, 1909, 81, 1—11, 72—91. Compare Abstr., 1908, ii, 1021).—II. The chemical nature of oxydases is uncertain, although numerous views on the question have been expressed. The present research relates to laccase prepared from *Medicago sativa*; it is found to be a mixture of the calcium salts of mono-, di-, and tri-basic hydroxy-acids, among which citric, malic, mesoxalic, and probably a good deal of glycollic acids were identified.

The Rhus laccase of Bertrand is different from the *Medicago* laccase, and is differently influenced by amount of acidity and certain reagents.

III. The activity of peroxydase can be estimated by the guaiacum reaction, and the influence of acidity and various reagents on the activity of a peroxydase from *Cochlearia armoracia* was determined. Exposure to 100° for less than a minute reduces its activity by one-half.

W. D. H.

The Alcoholic Ferment of Yeast-juice. IV. The Fermentation of Dextrose, Mannose, and Lævulose by Yeast-juice. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1909, B, 81, 336—347).—The influence of the addition of sodium phosphate on the rate of fermentation of dextrose, mannose, and lævulose by yeast-juice was investigated, and it was found that mannose behaves both in the presence and absence of phosphates in the same way as dextrose; lævulose, on the other hand, is fermented much more rapidly in the presence of phosphates, and the optimum concentration of these salts is higher. Lævulose has the property of inducing fermentation in solutions of dextrose and mannose which contain such an excess of phosphate that the fermentation is only proceeding very slowly. No similar property is possessed by dextrose or mannose.

S. B. S.

Attempts to Explain Cell-free Fermentation by means of Experiments with the Ultra-filter. A. VON LEBEDEF (Biochem. *Zeitsch.*, 1909, 20, 114—125).—The author has already shown that the rates of disappearance of sugar and formation of carbon dioxide during fermentation are not parallel (*ibid.*, 1908, 10, 456), and that sugar partly disappears when co-enzyme-free inactive expressed yeast-juice is employed. Further experiments have been made in which the co-enzyme has been separated by means of the Bechhold ultra-filter. The experiments showed that in the residue from the filtration (filtrans), sugar disappeared without appearance of the corresponding amount of carbon dioxide; the reducing power of the filtrate, on the other hand, remained unchanged even after eight days. A certain amount of phosphoric acid could be set free by hydrolysis, and in the filtrans the amount of sugar which could be set free by hydrolysis decreased with time, whereas in the case of the non-filtered juice it increased. These facts indicate that some form of sugar ester is formed as an intermediate product. The hot-water extract of yeast-juice was therefore subjected to ultra-filtration, and to the filtrate acetone was added. From the precipitate, which yielded phosphoric acid on hydrolysis, a precipitate with phenylhydrazine was obtained (m. p. 148—149°). Other derivatives were

also prepared, of which the preliminary investigation led to the surmise that this filtrate contains a phosphoric acid ester of dextrose, which is regarded as an intermediate product in sugar fermentation.

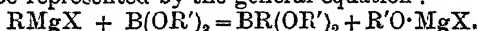
S. B. S.

**$\alpha$ -Siliconaphthoic Acid.** EUGEN KHOTINSKY (*Ber.*, 1909, 42, 3088—3089. Compare Abstr., 1908, i, 1032).— $\alpha$ -Siliconaphthoic acid has m. p.  $138^\circ$  after sintering at  $133^\circ$ . The m. p. previously given ( $239^\circ$ ) is incorrect (compare Melzer, Abstr., 1908, i, 967); ethyl ortho- $\alpha$ -siliconaphthoate has b. p.  $174-177^\circ/15-18$  mm.

J. J. S.

**Action of Organo-magnesium Compounds on Boric Esters.** EUGEN KHOTINSKY and M. MELAMED (*Ber.*, 1909, 42, 3090—3096).—Organo-magnesium compounds react with alkyl borates in much the same manner as with the ortho-esters of silicic acid (Abstr., 1908, i, 1032), only more readily.

The boric esters are best prepared by the action of alcohol on boric anhydride under pressure. The reaction with the magnesium compounds may be represented by the general equation:



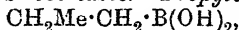
The resulting esters of alkylated boric acids are readily hydrolysed: methyl and ethyl esters by cold water, the *isoamyl* and *isobutyl* esters by warm water. The best yields of arylboric acids are obtained when *isobutyl* borate reacts with aryl magnesium halides, but the best yields of aliphylboric acids are obtained when methyl borate is used. These aliphylboric acids are unstable and excessively volatile. The methyl derivative,  $BMe(OH)_2$ , is so unstable that so far it has not been isolated in a pure state.

It has been noticed that methyl borate has a methylating action on magnesium phenyl bromide, the products consisting of toluene and phenylboric acid (compare Michaelis and Becker, Abstr., 1880, 396). *iso-Butyl phenylborate*,  $BPh(O \cdot C_4H_9)_2$ , is a colourless liquid, b. p.  $180-187^\circ/30-35$  mm.

*m-Tolylboric acid*,  $C_6H_4Me \cdot B(OH)_2$ , has m. p.  $137-140^\circ$ , and the *isobutyl* ester, has b. p.  $195-207^\circ/66$  mm. The acid reacts with a concentrated mercuric chloride solution, yielding *m*-tolyl mercuric chloride,  $C_6H_4Me \cdot Hg \cdot Cl$ .

*isoButyl benzylborate*,  $CH_2Ph \cdot B(O \cdot C_4H_9)_2$ , has b. p.  $189-196^\circ/36$  mm., and *benzylboric acid*,  $CH_2Ph \cdot B(OH)_2$ , m. p.  $161^\circ$ .

Ethylboric acid (Frankland, *Annalen*, 1862, 124, 142) sublimes readily at  $40^\circ$ , and has a sweet taste. *Propylboric acid*,



has m. p.  $74-75^\circ$ ; *isobutylboric acid*,  $CHMe_2 \cdot CH_2 \cdot B(OH)_2$ , m. p.  $104^\circ$ , and *isoamylboric acid*,  $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot B(OH)_2$ , m. p.  $101^\circ$ . Ammonium and sodium salts have been prepared from some of the acids; the ammonium salts are unstable, and readily evolve ammonia.

J. J. S.

## Organic Chemistry.

Action of Metallic Magnesium on Acetylene. J. NOVÁK (*Ber.*, 1909, 42, 4209—4213).—When magnesium powder is heated in a stream of pure acetylene, reaction begins to take place at a temperature of about 450°, carbon being deposited, and a mixture of magnesium acetylide and allylide formed. The product formed reacts violently with water, a mixture of acetylene and allylene being evolved. These two gases were identified by making various derivatives.

T. S. P.

Aliphatic Compounds of Polyvalent Iodine. III. Derivatives of Ethylene with Tri- and Quinque-valent Iodine. JOHANNES THIELE and HERMANN HAAKE (*Annalen*, 1909, 369, 131—147. Compare *Abstr.*, 1905, i, 735; this vol., i, 879).—Iodochlorides and the corresponding iodoso-derivatives may be readily obtained from  $\alpha\beta$ -di-iodoethylene and  $\alpha$ -chloro- $\beta$ -iodoethylene, the compounds derived from the latter being far more stable than those prepared from the former. Iodosochloroethylene when boiled with water yields chloriodoxyethylene, the first iodoxy-compound in the aliphatic series to be prepared.

Attempts to prepare bischlorovinylidonium hydroxide by the action of silver oxide or alkali oxides on a mixture of iodoso- and iodoxy-chloroethylene were unsuccessful. Willgerodt and his co-workers (*Abstr.*, 1895, i, 635; 1900, i, 338, 432; 1902, i, 17, 18; 1904, i, 483, 657) have shown that aliphatic-aromatic iodonium salts may be prepared by the action of aromatic iodochlorides on acetylene silver chloride; for example, phenyl iodochloride is said to react with acetylene silver chloride, yielding phenyldichloroethylidonium chloride. It is found, however, that chloroethylene iodochloride reacts with acetylene silver chloride, yielding dichlorovinylchlorovinylidonium chloride, and not dichloroethylchlorovinylidonium chloride, as would be expected if the reaction follow the course depicted by Willgerodt. The work of this author was repeated, therefore, with the result that the compounds described by him as dichloroethylidonium compounds are found to be dichlorovinyl compounds.

Experiments which were performed with the object of preparing iodochlorides from acetyl iodide and benzoyl iodide led only to the discovery of a better method of preparing the first-named substance. Benzoyl iodide cannot be prepared in the manner described by Liebig and Wöhler; it is probable that this compound has not yet been prepared.

*Iodoethylene iodochloride*,  $\text{CHI}:\text{CH}:\text{ICl}_2$ , prepared by passing chlorine into a solution of di-iodoethylene in chloroform cooled in a freezing mixture, crystallises in lemon-yellow needles and decomposes at about 37°; it is very unstable, and cannot be kept; when treated with a

cold 20% aqueous solution of sodium carbonate, it yields  $\beta$ -iodo- $\alpha$ -iodosoethylene,  $\text{CHI}:\text{CH}:\text{IO}$ , a very unstable, slightly yellow, amorphous substance, which explodes slightly at about  $62^\circ$ .

*Chloroethylene iodochloride*,  $\text{CHCl}:\text{CH}:\text{ICl}_2$ , crystallises in lemon-yellow needles, m. p.  $75-77^\circ$ , and is converted by a 20% aqueous solution of sodium carbonate into  $\beta$ -chloro- $\alpha$ -iodosoethylene,  $\text{CHCl}:\text{CH}:\text{IO}$ , an unstable, amorphous, pale yellow powder, which explodes at about  $63^\circ$ , and forms an *acetate*,  $\text{CHCl}:\text{CH}:\text{I}(\text{OAc})_2$ , colourless leaflets, m. p.  $96^\circ$ , and *chromate*, an unstable, yellow powder.  $\beta$ -Chloro- $\alpha$ -iodoxyethylene,  $\text{CHCl}:\text{CH}:\text{IO}_2$ , prepared by treating chloroethylene iodochloride with water at  $72-75^\circ$ , forms white crystals, which explode with great violence at  $135^\circ$ , also when struck or rubbed on a porous plate; it is decomposed by aqueous sodium hydroxide and by water at  $100^\circ$ , yielding acetylene.

*Dichlorovinylchlorovinylidonium chloride*,  $\text{CHCl}:\text{CH}:\text{ICl}:\text{CCl}:\text{CHCl}$ , crystallises in short, white needles, and decomposes at  $207^\circ$ ; the following salts are obtained from the chloride by double decomposition: *aurichloride*,  $\text{C}_4\text{H}_3\text{Cl}_3\text{I} \cdot \text{AuCl}_4$ , golden-yellow needles, m. p.  $111^\circ$  (decomp.); *platinichloride*,  $(\text{C}_4\text{H}_3\text{Cl}_3\text{I})_2\text{PtCl}_6$ , brownish-red granules, m. p.  $93-94^\circ$  (decomp.); *bromide*, white powder, volatile at about  $200^\circ$  (decomp.); *iodide*, white powder, which rapidly turns yellow, m. p.  $97^\circ$  (decomp.).

*Phenyldichlorovinylidonium bromide*,  $\text{C}_6\text{H}_5\text{Cl}_2\text{I} \cdot \text{Br}$ , is a white powder, volatile at  $162^\circ$  (decomp.). W. H. G.

**Aliphatic Compounds of Polyvalent Iodine. IV. Decomposition of Aliphatic and Aliphatic-Aromatic Iodonium Compounds.** JOHANNES THIELE and ANNA UMNOFF (*Annalen*, 1909, 369, 147-149).—Phenyldichlorovinylidonium bromide, when heated at  $180^\circ$ , decomposes into iodobenzene and  $\alpha\beta$ -dichloro- $\alpha$ -bromoethylene, and, when acted on by cold dilute aqueous sodium hydroxide, yields chloroacetylene, iodobenzene, and hypochlorous acid.

Dichlorovinylchlorovinylidonium bromide decomposes in an analogous manner when treated similarly. W. H. G.

**Aliphatic Compounds of Polyvalent Iodine. V. Simple Alkyl Iodochlorides.** JOHANNES THIELE and WILLI PETER (*Annalen*, 1909, 369, 149-156).—An account of part of the work described in this paper has already appeared (compare Abstr., 1905, i, 735).

The first representative of a new class of compounds, namely, *methyl iodobromide*,  $\text{CH}_3\text{I} \cdot \text{Br}$ , has been prepared by the action of bromine on methyl iodide in light petroleum at about  $-70^\circ$ ; it crystallises in glistening, orange-yellow leaflets, and decomposes at about  $-45^\circ$ . *Phenyl iodobromide* appears to be formed by acting on iodobenzene with bromine in light petroleum.

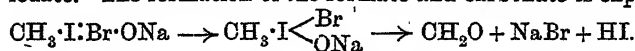
Alkyl iodides also combine with iodine at very low temperatures, yielding brown, crystalline *polyiodides*, probably tri-iodides,  $\text{RI}_3$ .

Ethyl iodochloride is a faintly yellow substance, which decomposes at  $-36^\circ$ . Methylene iodide dichloride,  $\text{CH}_2\text{I} \cdot \text{ICl}_2$ , is a yellow powder, and decomposes at  $-11.5^\circ$ . W. H. G.

**Reactions of Hypohalites with Organic Compounds.**  
**Reactions with Derivatives of Methane.** WILLIAM M. DEHN  
 (*J. Amer. Chem. Soc.*, 1909, 31, 1220—1233).—Although numerous reactions between hypohalites and organic compounds have been recorded, there has not hitherto been any attempt made to study the whole subject systematically. The author has therefore undertaken an investigation with the object of elucidating the mechanism of the reaction between hypohalites and organic compounds generally. The present paper gives an account of experiments made with compounds containing one atom of carbon.

It is shown that these reactions cannot be explained on the basis of ionisation or of methylene dissociation, but that they can be satisfactorily accounted for by the author's theory of molecular coalescence (*Abstr.*, 1908, i, 721).

Methane is not affected by sodium hypobromite at the ordinary temperature. Methyl iodide reacts with sodium hypobromite with formation of sodium iodide, iodate, periodate, formate, and carbonate, and the sodium formate, if left for some days with excess of the hypobromite, is completely oxidised to the carbonate according to the equations:  $\text{CH}_3\text{I} + 2\text{NaOBr} + 2\text{NaOH} \rightarrow \text{H}\cdot\text{CO}_2\text{Na} + \text{NaI} + 2\text{NaBr} + \text{H}_2\text{O}$  and  $\text{H}\cdot\text{CO}_2\text{Na} + \text{NaOBr} + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{NaBr} + \text{H}_2\text{O}$ . The sodium iodide is oxidised by the hypobromite to the iodate and periodate. The formation of the formate and carbonate is explained thus



The following reactions show that the hypohalites afford a general method of formation of tetrahalogenmethanes. Chloroform reacts with sodium hypochlorite with production of sodium chloride formate, and carbonate, and carbon tetrachloride. A similar reaction takes place with sodium hypobromite, with formation of trichlorobromomethane and small quantities of dichlorodibromomethane and tetrabromomethane. With sodium hypoiodite, trichloroiodomethane and dichlorodi-iodomethane are produced.

Bromoform, when treated with sodium hypochlorite, yields chlorotribromomethane, tetrabromomethane, and possibly dichlorodibromomethane, whilst with sodium hypobromite, it gives tetrabromomethane. When iodine is added gradually to a mixture of bromoform and sodium hydroxide solution, *tribromoiodomethane* is obtained as a golden-yellow, crystalline precipitate, which darkens and decomposes at 35°; if a large quantity of iodine is used, iodoform and tetraiodomethane are also produced.

Iodoform reacts with sodium hypochlorite to form a mixture of brick-red and white crystals, which could not be purified. With sodium hypobromite, it yields *bromotri-iodomethane*, m. p. 113°, as a brick-red, amorphous solid.

When sodium hypobromite is added to a dilute aqueous solution of methyl alcohol, tetrabromomethane is immediately precipitated; this reaction can be employed for the detection of wood-spirit in methylated spirit and other mixtures. If an excess of dilute methyl alcohol is added gradually to the hypobromite solution, bromoform and tetrabromomethane are produced. On adding the hypobromite to ex-

cess of dilute methyl alcohol and distilling the mixture, methylal is obtained in the distillate, showing that formaldehyde is formed as an intermediate product of the reaction between methyl alcohol and the hypobromite. When a solution of methyl alcohol containing potassium iodide is treated with sodium hypobromite, iodoform, tetraiodomethane, and formic acid are produced.

Formaldehyde and trioxymethylene are converted by sodium hypobromite into sodium formate or carbonate, depending on the quantity of the hypobromite added. Formic acid is converted by the reagent into sodium carbonate.

Carbon disulphide reacts with sodium hypobromite to form sodium sulphide, sulphate, formate, and carbonate.

Potassium cyanide is oxidised by sodium hypobromite with formation of cyanate, formate, and carbonate. When potassium cyanate is treated with the reagent, nitrogen is slowly evolved, and formate and carbonate are produced. Potassium thiocyanate gives sulphate and cyanate. Sodium ferrocyanide is converted into the ferricyanide. When sodium ferricyanide is boiled with sodium hypobromite, a deep brownish-red precipitate is obtained, consisting of a mixture of a basic ferric formate and ferric oxide.

When methylamine is treated with the hypobromite, nitrogen is slowly evolved and tetrabromomethane is produced, methyl-bromoamine or -dibromoamine being formed as an intermediate product. Schestakoff (*Abstr.*, 1905, i, 332) has shown that when sodium hypochlorite reacts with carbamide, hydrazine is formed as an intermediate compound. It is pointed out that the formation of this substance can be easily explained as follows:  $(\text{NH}_2)_2\text{C}:\text{O}:\text{Br}\cdot\text{ONa} \rightarrow (\text{NH}_2)_2\text{C}(\text{OBr})\cdot\text{ONa} \rightarrow \text{N}_2\text{H}_4 + \text{CO}_2 + \text{NaBr}$ . Ammonia, like carbamide, gives a quantitative yield of nitrogen. Guanidine and semicarbazide yield about two-thirds of their nitrogen, whilst urethane furnishes only a very small quantity of the gas. It is evident from these reactions that the evolution of nitrogen is not determined merely by the presence of an amino-group, but that it depends very largely on the other groups in the compound. The dissimilarity of the reactions with these amino-compounds can be best explained by assuming the formation of different aggregates, such as  $\text{NH}_2\text{Br}(\text{ONa})$ ,  $\text{OH}\cdot\text{NH}_2\text{Br}(\text{ONa})$ , and  $\text{NH}_2\text{MeBr}(\text{ONa})$ , which vary in stability or in the way in which they decompose. E. G.

**Specific Gravities of Alcoholic Solutions. I. Mixtures of Methyl Alcohol with Water.** ANTONY G. DOROSCHEWSKY and M. S. ROSCHDESTVENSKY (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 977—996).—After reviewing previous work on the specific gravities of methyl alcohol and its aqueous mixtures, the authors give the results of their determinations at 15°/15° for a series of twenty-five mixtures varying in concentration from 0% to 100%. From these results they calculated the values of  $D_{15}^{15}$  for each integral percentage of alcohol from 0 to 100 in two different ways: (1) by graphic interpolation, and (2) by means of the contraction occurring on mixing. The mean difference between the two sets of numbers thus obtained is 0.00002. For absolute methyl alcohol,  $D_{15}^{15}$  has the value 0.79647 (compare

Young and Fortey, *Trans.*, 1902, 81, 735; Klason and Norlin, *Abstr.*, 1906, i, 921). T. H. P.

**Electrolytic Oxidation of Ethyl Alcohol to Acetic Acid.** PAUL ASKENASY, R. LEISER, and N. GRÜNSTEIN (*Zeitsch Elektrochem.*, 1909, 15, 846—860).—The experiments are made with the object of testing the economic possibility of the process. Using platinum gauze electrodes 3 mm. apart, and a solution containing about 190 grams of alcohol and 27 to 30 grams of sulphuric acid in 750 c.c., it is found that a current density of about 0.2 ampere per sq. cm. can be maintained with 4.5 volts. At first considerable quantities of ethyl acetate are formed, but as the alcohol is oxidised by electrolysis, this diminishes. Aldehyde also escapes, and is condensed in a small subsidiary cell and there oxidised. The yield appears to be rather better at 30° or 40° than it is at lower temperatures. In the best circumstances the current efficiency is about 78%, and the yield on the alcohol about 80%. Other experiments made with a cheap 8% alcohol obtained by the direct fermentation of the expressed juice of sugar beets gave even better results; a little chromium sulphate was added to the solution to act as an oxygen carrier. T. E.

**Ether-like Compounds. I. Ether Alcohols of the Type  $R \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ .** M. H. PALOMAA (*Ber.*, 1909, 42, 3873—3878).—To prepare ethylene glycol monomethyl ether,  $OMe \cdot CH_2 \cdot CH_2 \cdot OH$ , sodium is dissolved in ethylene glycol under special conditions, the sodium glycol oxide brought into reaction with methyl iodide, and the product purified by fractional distillation. It has b. p. 124.9°/767.5 mm., is a colourless liquid with an odour resembling impure methyl alcohol, and is miscible with water;  $D_{15}^{15}$  0.96928. The acetate,  $OMe \cdot CH_2 \cdot CH_2 \cdot OAc$ ,

has b. p. 144.5—145°; the propionate,  $OMe \cdot CH_2 \cdot CH_2 \cdot O \cdot COEt$ , has b. p. 159.56°/741.9 mm.,  $D_{15}^{15}$  0.9867. The butyrate has b. p. 177.5°/767.8 mm. The benzoate,  $OMe \cdot CH_2 \cdot CH_2 \cdot O \cdot OBz$ , has b. p. 254—256°/760 mm.,  $D_{15}^{15}$  1.1067.

Ethylene glycol monoethyl ether,  $OEt \cdot CH_2 \cdot CH_2 \cdot OH$ , prepared similarly to the methyl derivative, has b. p. 134.8°/748 mm.,  $D_{15}^{15}$  0.93535, agreeing with the constants given by Demole (*Ber.*, 1876, 9, 745). Ethylene glycol monopropyl ether,  $OPr \cdot CH_2 \cdot CH_2 \cdot OH$ , has b. p. 150.2°/753 mm.,  $D_{15}^{15}$  0.91432. Ethylene glycol monoallyl ether,  $CH_2 \cdot CH \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$ ,

has b. p. 159°/755 mm.,  $D_{15}^{15}$  0.96095.

The acetic, propionic, butyric, isobutyric, and benzoic acid esters of the last three glycol ethers are colourless liquids, easily obtained by the pyridine method, and distil without decomposition with the exception of the esters of the monoallyl ether. E. F. A.

**Purification of Glycerol Dinitrate.** CONRAD CLAESSEN (D.R.-P. 210990).—When glycerol dinitrate is exposed for some hours in an atmosphere containing 70—80% of moisture (or treated with damp infusorial earth), frozen, and triturated with a glass rod, a crystalline hydrate,  $3C_3H_5(OH)(ONO_2)_2 \cdot H_2O$ , colourless prisms, m. p. 25°, is formed;

when heated at 40° it loses its water of crystallisation, regenerating liquid glycerol dinitrate.

F. M. G. M.

**Lipoids. VII. Kephalin.** SIGMUND FRÄNKEL and ERNST NEUBAUER (*Biochem. Zeitsch.*, 1909, 21, 321—336).—The kephalin was prepared by extracting human brains, dried rapidly at 100°, first with cold and then with hot alcohol. The residue was extracted with light petroleum, and alcohol was then added to this solution after concentration. The precipitate thus formed was extracted with hot alcohol, and then redissolved in hot petroleum, from which a galactoside separated on cooling; this was separated by centrifuging, and the kephalin was then precipitated from the solution by alcohol. From the crude kephalin, purer preparations were made (I) by suspending the crude substance in water, with which it forms a mucilagenous solution, and precipitating therefrom with hydrochloric acid and hardening the precipitate with acetone; (II) by repeated solution of this precipitate in light petroleum and precipitation therefrom with alcohol; (III) by precipitation of the mucilagenous aqueous solution with sodium sulphate. The kephalin forms with water a colloidal solution, from which it can be precipitated by various salts, the precipitating power of several of which has been quantitatively investigated by the author. The purest preparation contained 62.05% C, 9.85% H, 1.69% N, 3.45% P, and 1.86% CH<sub>3</sub> (determined by the method of Herzig and Mayer). The ratio of P:N:CH<sub>3</sub> according to these numbers is 1:1.07:0.98. The melting point of this preparation was 175°; it was lævorotatory and unsaturated (iodine number = 280).

S. B. S.

**Lipoids. VIII. The Scission Products of Kephalin** SIGMUND FRÄNKEL and LUDWIG DIMITZ (*Biochem. Zeitsch.*, 1909, 21, 337—347).—The hydrolysis was carried out with alcoholic hydrochloric acid. As products of hydrolysis were obtained: acids, which probably consisted of a mixture of palmitic and stearic acids; and a glycerophosphoric acid, which was dextrorotatory, and differs in this respect from the glycerophosphoric acid from egg-lecithin, which is lævorotatory.

S. B. S.

**Electrolysis of Carboxy-acids.** FELIX KAUFLEDER and C. HERZOG (*Ber.*, 1909, 42, 3858—3873).—Three different theories have been put forward to account for the formation of ethane in the electrolysis of solutions of sodium or potassium acetate, namely: (1) the discharged acetanion breaks up into carbon dioxide and methyl, two methyls then uniting to form ethane (Abstr., 1891, 1192); (2) two discharged acetanions combine to form acetyl peroxide, which then breaks up into ethane and carbon dioxide (Abstr., 1897, i, 317); (3) two discharged acetanions form acetic anhydride and oxygen, and then further changes take place, resulting in the formation of ethane and carbon dioxide. The authors produce evidence in favour of the first theory.

A solution of potassium acetate, containing either free iodine or potassium iodide, was electrolysed in a divided cell, and the anode gases could be passed over moist red phosphorus in order to absorb

any iodine carried over, and then through an alcoholic solution of dimethylaniline, which, if the methyl radicle is liberated, would be converted into phenyltrimethylammonium iodide. This compound was actually obtained by the authors. It is further shown that the methyl iodide did not result from an iodoacetic acid which might be formed as an intermediate product of the electrolysis of the above solution. Prolonged electrolysis of a solution of potassium acetate containing iodine did not give rise to iodoacetic acid.

The second theory was disproved by submitting acetyl peroxide to the action of iodine; methyl iodide was not formed. Foerster and Piguet (Abstr., 1904, i, 965) were in favour of this theory, because they found that there was a considerable anodic resistance to the passage of the current, but by experiments on the electrolysis of sulphuric acid solutions the authors show that this is a characteristic of platinum electrodes (anode or cathode), and not of an acetate electrolyte.

The third theory is untenable, because, according to it, the oxidation or introduction of halogen would be expected to take place to a much greater extent than is actually the case.

The electrolysis of a solution of sodium chloroacetate gave rise to the anodic formation of chlorine, carbon monoxide, carbon dioxide, and hydrogen chloride; as subsidiary products were also formed methylene chloride and chloromethyl chloroacetate. The mechanism of the reaction is probably as follows: the discharged chloroacetanion decomposes, for the most part, into carbon monoxide, chlorine, and formaldehyde. The hydrogen chloride is then produced by the action of chlorine on the formaldehyde or the carbon monoxide. Carbon dioxide also results from the ordinary decomposition of the discharged chloroacetanion; this would leave the residue  $\text{CH}_2\text{Cl}$ , which either combines with chlorine to form methylene chloride, or with the residue  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{O}$  to form chloromethyl chloroacetate. This latter compound separates as a heavy oil during the electrolysis. Formaldehyde was also identified. No trace of ethylene dichloride was found.

Electrolysis of a solution of sodium bromoacetate gave rise to the anodic formation of bromine, carbon monoxide, carbon dioxide, and oxygen as primary products. Methyl bromide was also isolated, and also small quantities of an oil, which was probably bromomethyl bromoacetate.

In the electrolysis of sodium iodoacetate, the only non-gaseous products which could be isolated were iodine and methylene iodide.

From sodium dichloroacetate, dichloromethyl dichloroacetate was obtained, which distilled at  $93-95^\circ/33$  mm.;  $D_4^{20}$  1.588. In the electrolysis of salts of the aromatic acids, the discharged anion regenerates the acid. In order to see if the difference in behaviour from that of the aliphatic acids is due to the stronger acid character of the phenyl group, or to a special chemical influence of this group, the potassium salt of *p*-dimethylaminobenzoic acid was electrolysed; the acid was regenerated. The acid is also regenerated from the salts of phenylacetic and acetylmandelic acids. Walker (Trans., 1896, 69, 1279) obtained hydrobenzoin by the electrolysis of mandelic acid,

but, since he worked without a diaphragm, it was probably formed by the interaction of the anodic and cathodic products.

Acetylmandelic (*α*-acetoxyphenylacetic) acid was prepared from acetic anhydride and mandelic acid. It crystallises with  $\frac{1}{2}$ H<sub>2</sub>O, and has m. p. 52°, or when anhydrous, m. p. 76°. T. S. P.

Salts of an Acetatoferri-base and of Two Acetatochromi-ferri-Bases. III. RUDOLF F. WEINLAND and E. GUSSMANN (*Ber.*, 1909, 42, 3881—3894. Compare Abstr., 1908, i, 847; this vol., i, 757).—Acetatoferri-salts have now been prepared of similar composition to the acetatochromo-salts previously described. Solutions of chromic acid and ferric chloride in acetic acid also yield mixtures of salts of bases containing both chromium and iron. All the salts of these bases with any given acid are isomorphous, and some of the salts previously described are certainly isomorphous mixtures. The dichroism observed in certain cases is a sign of the presence of isomorphous mixtures.

Of the triferri-base, the following salts have been prepared: dichromate-acetate,  $\left[ \text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{Cr}_2\text{O}_7$ , formerly described as containing only 1H<sub>2</sub>O. The *mono-acetate*,  $\left[ \text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{OAc} \cdot \text{H}_2\text{O}$ , obtained by dissolving ferric hydroxide, freshly precipitated in the cold, in 95% acetic acid, and evaporating over sulphuric acid, forms dark orange, rhombic leaflets, slowly soluble in cold water, rapidly in hot, sparingly soluble in glacial acetic acid. The *diacetate*,  $\left[ \text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ \text{OH} \end{smallmatrix} \right] (\text{OAc})_2$ , prepared by heating the mono-acetate with excess of acetic acid to boiling for twelve hours, forms minute, orange tablets. The *platinichloride*,  $\left[ \text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \frac{1}{2} \text{PtCl}_6 \cdot 5\text{H}_2\text{O}$ , prepared by adding platinic chloride to a solution of the mono-acetate, forms minute bundles of prisms, soluble in water. The *stannichloride*,  $\left[ \text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \frac{1}{2} \text{SnCl}_6 \cdot 5\text{H}_2\text{O}$ , prepared from the acetate and sodium chlorostannate, is similar in character, whilst the *nitrate*,  $\left[ \text{Fe}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{NO}_3 \cdot 4\text{H}_2\text{O}$ , from the acetate and lithium nitrate, forms minute, orange tablets.

Salts of the dichromiferri-base are prepared by mixing the two hydroxides in the required proportions, dissolving in acetic acid, and precipitating. The *platinichloride*,  $\left[ \text{Cr}_2\text{Fe} \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \frac{1}{2} \text{PtCl}_6 \cdot 5\text{H}_2\text{O}$ , forms minute, reddish-violet prisms, and the *stannichloride* resembles it closely. The *chloride*,  $\left[ \text{Cr}_2\text{Fe} \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{Cl} \cdot 6\text{H}_2\text{O}$ , obtained by the aid of lithium chloride, crystallises from water containing lithium chloride in rhombic, violet prisms. The *chromate*,  $\left[ \text{Cr}_2\text{Fe} \begin{smallmatrix} (\text{OAc})_6 \\ \text{OH}_2 \\ \text{OH} \end{smallmatrix} \right] \text{CrO}_4 \cdot 4\text{H}_2\text{O}$ , forms large, black plates.

The *mono-acetate* of the chromidiferri-base,  $\left[ \text{CrFe}_2 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] \text{OAc} \cdot \text{H}_2\text{O}$ ,

forms sparingly soluble, microscopic, brownish-red leaflets. The *platinichloride*,  $\left[\text{CrFe}_2\left(\frac{\text{OAc}}{\text{OH}}\right)_6\right]\frac{1}{2}\text{PtCl}_6\cdot 5\text{H}_2\text{O}$ , is brownish-red, and the *chloride*,  $\left[\text{CrFe}_2\left(\frac{\text{OAc}}{\text{OH}}\right)_6\right]\text{Cl}\cdot 8\text{H}_2\text{O}$ , forms black prisms.

The aqueous solutions of all these salts have an acid reaction. In the presence of ferric chloride, ferrichlorides are formed. Ammonia does not precipitate iron or chromium from the solutions unless heated.

The characteristic colours of these salts (deep violet for the  $\text{Cr}_2\text{Fe}$  and reddish-brown for the  $\text{CrFe}_2$  salts) indicate that they are not isomorphous mixtures of salts of the green  $\text{Cr}_3$  and red  $\text{Fe}_3$  bases.

C. H. D.

**Ethyl Acetate.** JOSEF HABERMANN and H. BREZINA (*J. pr. Chem.*, 1909, [ii], 80, 349—354).—A mixture of 400 grams of 96 volume % alcohol, 240 grams of glacial acetic acid, and 160 grams of anhydrous copper sulphate is kept at the ordinary temperature for twenty-four hours, and is then heated for twelve to fourteen hours on the water-bath, in both cases with frequent shaking. The liquid is decanted from the copper sulphate, heated again for ten hours with another 50 grams of anhydrous copper sulphate, and then distilled after the removal of the metallic salt. The distillate is fractionally distilled, and the main fraction, b. p.  $70-72^\circ$ , is repeatedly washed with saturated brine, dried by ignited magnesium sulphate, and again distilled. The distillate has b. p.  $70-72^\circ$ , and a vapour density corresponding with that of an equimolecular compound of ethyl alcohol and ethyl acetate. By prolonged shaking with calcium chloride, the ethyl alcohol seems to be removed, for the liquid now has b. p.  $77^\circ$  and a vapour density corresponding with that of ethyl acetate.

A small quantity of the same compound, b. p.  $70-72^\circ$ , can be isolated from commercial ethyl acetate by systematic fractionation.

C. S.

**Production of Alkyl Chloroacetates from Dihalogenated Vinyl Ethers.** GEORGES IMBERT and CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE (D.R.-P. 212592. Compare this vol., i, 453, 694).—The reaction between dihalogenated vinyl ethers and alcohol takes place at the ordinary temperature in the absence of moisture and in the presence of a catalyst, such as aluminium chloride. Methyl chloroacetate is prepared from dichlorovinyl ether and methyl alcohol, and ethyl bromoacetate from dibromovinyl ether and alcohol.

F. M. G. M.

**Some Organic Compounds of Glucinum.** CHARLES L. PARSONS and GEORGE J. SARGENT (*J. Amer. Chem. Soc.*, 1909, 31, 1203—1206).—It has been shown by Parsons (Abstr., 1905, ii, 34; 1906, i, 479; 1908, ii, 105) that a definite compound cannot be obtained by saturating an acid with glucinum hydroxide or carbonate. The so-called basic salts obtained in this way are not definite compounds, but consist of solid solutions of the normal salts in the hydroxide.

Glassmann (Abstr., 1908, i, 120) and Tanatar and Kurovski (Abstr., 1908, i, 166) have described a number of glucinum compounds with organic acids. A study has now been made of all the salts which these authors prepared by saturating the acid with glucinum hydroxide or carbonate, and it is shown that the supposed compounds are merely indefinite mixtures or solid solutions.

A crystalline *trichloroacetate*,  $\text{Gl}(\text{C}_2\text{O}_2\text{Cl}_3)_2 \cdot 2\text{H}_2\text{O}$ , can be obtained by dissolving glucinum carbonate in excess of trichloroacetic acid.

Normal glucinum salts of acids having a much lower ionisation constant than that of oxalic acid have not been made, and it is improbable that a sufficiently high concentration of hydrogen ions can be obtained to enable them to separate as definite compounds from aqueous solutions. E. G.

#### Aliphatic Nitro-compounds. VI. Free Nitroacetic Acid.

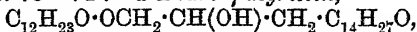
WILHELM STEINKOPF (*Ber.*, 1909, 42, 3925—3929. Compare this vol., i, 216, 559).—It is possible to prepare the sodium or potassium salts of nitroacetic acid in one operation from nitromethane by the action of sodium or potassium hydroxide. Nitromethane is allowed to drop into the alkali, and the mixture ultimately boiled for ten minutes. On cooling, the nitroacetate crystallises.

*Nitroacetic acid*,  $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is obtained by acting on a finely divided suspension of potassium nitroacetate in dry ether with dry hydrogen chloride gas, removal of the salt by filtration, and evaporation of the ether. Nitroacetic acid may be crystallised from chloroform or benzene without decomposition in long needles, m. p.  $87-89^\circ$  (slight decomp.). Larger quantities explode when melted. The acid is rapidly decomposed by water into carbon dioxide and nitromethane, but it can be in part recovered from aqueous solution if this be rapidly extracted with ether. It forms colourless, crystalline salts with primary amines. *Aniline nitroacetate* yields silvery, glistening plates; *phenylhydrazine nitroacetate* has m. p.  $58^\circ$  (decomp.). Attempts to prepare nitroacetyl chloride were not successful. E. F. A.

**Synthesis of the Triple Mixed Glycerides.** ADOLF GRÜN and A. VON SKORNIK (*Ber.*, 1909, 42, 3750—3759).—An account of the synthesis of glycerides containing three different acid groups, namely, those derived from lauric, myristic, and stearic acids.

$\alpha$ -Chlorohydrin and lauryl chloride yield  $\gamma$ -*lauro- $\alpha$ -chlorohydrin*,  $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_{12}\text{H}_{23}\text{O}$ , a pale yellow, mobile oil.  $\gamma$ -*Lauro- $\alpha\beta$ -dichlorohydrin*, obtained by boiling the laurochlorohydrin, dissolved in carbon tetrachloride, with phosphorus pentachloride in a current of hydrogen, is a bright yellow, fairly mobile liquid. The dichlorohydrin produced on saponifying it with alcoholic potash could not be identified, but the constitution of the substance follows from its conversion by the action of silver nitrite (compare Abstr., 1907, i, 464) into  $\alpha$ -*monolaurin*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_{12}\text{H}_{23}\text{O}$ , which forms shining laminae of m. p.  $52^\circ$ . When the substance has solidified after fusion, it has m. p.  $40-41^\circ$ . It does not give a phenylurethane with phenylcarbimide, thus differing from  $\beta$ -monolaurin.  $\beta$ -*Monolaurin*, from  $\beta$ -*lauro- $\alpha\gamma$ -dichlorohydrin*, has m. p.  $58.5^\circ$ .  $\beta$ -*Monolaurin phenyl-*

carbamate (from  $\beta$ -monolaurin and phenylcarbimide) forms white crystals of m. p. 73—74°. *a*-Lauro- $\gamma$ -myristin,



is prepared by heating together at 140°  $\gamma$ -lauro- $\alpha$ -chlorohydrin and potassium myristate. It forms very small, white crystals, m. p. 40—42°, or, after having been once melted, 34—35°. *a*-Lauro- $\gamma$ -myristo- $\beta$ -stearin,  $\text{C}_{12}\text{H}_{23}\text{O}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{O}\cdot\text{C}_{18}\text{H}_{35}\text{O})\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_{14}\text{H}_{27}\text{O}$ , is formed by heating the preceding compound with the calculated amount of stearyl chloride for one hour on the water-bath. It forms small, white, very soft crystals, m. p. 37—38°, or, after having been melted, 35°. *a*-Stearo- $\gamma$ -chlorohydrin (from stearyl chloride and  $\alpha$ -chlorohydrin) forms white, granular crystals, m. p. 48—49°, or, after having been fused, 39—40°.  $\gamma$ -Lauro- $\alpha$ -stearin, prepared by heating the preceding compound with potassium laurate for ten hours at 120° in an atmosphere of hydrogen, forms dense, granular, white crystals, m. p. 52—53°, or, after solidification, 45°.  $\gamma$ -Lauro- $\beta$ -myristo- $\alpha$ -stearin is prepared in the same way as the lauromyristostearin above described; it forms dull white, soft, crystalline grains, m. p. 48—49° (after solidifying, 44—45°). The m. p. sinks, on keeping, to 46°.  $\gamma$ -Myristo- $\alpha$ -stearin is obtained in white, granular crystals by heating together stearo-chlorohydrin and potassium myristate; it has m. p. 52—53° (softening at 47°), or, after fusion, at 44°.  $\beta$ -Lauro- $\gamma$ -myristo- $\alpha$ -stearin is prepared by acting on the above diglyceride with lauryl chloride; the crystals are white and yellow, and are not well-defined; they have m. p. 42°, or, after fusion, 32°. These three isomeric triglycerides show great similarity in physical properties, but the differences in m. p. show them to be distinct substances. The melting points of mixtures of them are not very sharp, but lie in all cases between those of the components, as was also the case with the "doubly mixed" triglycerides.

The synthetic methods described in the paper are to be extended to the production of optically active glycerides.

R. V. S.

**Preparation of Chlorohydroxy-acids and their Glycerides.** CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE and GEORGES IMBERT (D.R.-P. 212001).—Oleic, linoleic, and erucic acids are converted into the corresponding chlorohydroxy-saturated acids by treatment with chlorine in the presence of excess of either sodium carbonate or sodium hydrogen carbonate.

F. M. G. M.

**Some Transformations of Ricinoleic Acid.** ADOLF GRÜN (Ber., 1909, 42, 3759—3763).—The action of sulphuric acid on ricinoleic acid as described by Chonowsky (this vol., i, 760) differs considerably from the results obtained by others, including the author. His fraction of b. p. 73—74° is probably a mixture of the isomerides of b. p. 60.5° and 90°. The author maintains his former statements, and has recently repeated the preparation of the dihydroxystearic acids on a larger scale, with the result that he has isolated from the fourth fraction a substance in the form of small, white needles, m. p. 126°, which from its properties is the fourth isomeric *dihydroxystearic acid*. Chonowsky's substance, m. p. 115—116°, is also probably a mixture. Other discrepancies may be due to the formation of internal anhydrides,

which is characteristic of hydroxy-acids of high molecular weight. For instance, the author finds that ricinoleic acid when treated with acetic anhydride yields, not acetylricinoleic acid, but *acetylricinoleylricinoleic acid*,  $\text{OAc} \cdot \text{C}_{17}\text{H}_{32} \cdot \text{CO} \cdot \text{O} \cdot \text{C}_{17}\text{H}_{32} \cdot \text{CO}_2\text{H}$ . R. V. S.

**$\epsilon$ -Nitro- $\gamma$ -ketohehoic Acid and its Transformation Products.** JOHANNES THIELE and HERMANN LANDERS (*Annalen*, 1909, 369, 300—310).— *$\epsilon$ -Nitro- $\gamma$ -ketohehoic acid*,  $\text{NO}_2 \cdot [\text{CH}_2]_2 \cdot \text{CO} \cdot [\text{CH}_2]_2 \cdot \text{CO}_2\text{H}$ , prepared by boiling furfurylidenenitroethane with fuming hydrochloric acid, crystallises in glistening, white needles, m. p. 91—92°; the *methyl ester* is an oil, which decomposes when heated; the *semicarbazone*,  $\text{C}_7\text{H}_{12}\text{O}_5\text{N}_4$ , forms small, white needles, m. p. 167° (decomp.). The acid is oxidised by an aqueous solution of potassium permanganate or by strong nitric acid, yielding oxalic acid and succinic acid; when heated with fuming hydrochloric acid in a sealed tube at 150°, it yields

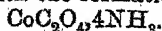
*3-chloroisooxazole-5-propionic acid*,  $\text{N} \begin{array}{c} \text{---} \text{O} \\ \parallel \\ \text{Cl} \cdot \text{CH} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which

crystallises in glistening, white leaflets, m. p. 84—85°, and forms a *methyl ester*,  $\text{C}_7\text{H}_9\text{O}_3\text{NCl}$ , crystallising in white needles, m. p. 40°. *3-Bromoisooxazole-5-propionic acid*,  $\text{C}_6\text{H}_8\text{O}_3\text{NBr}$ , prepared by heating  $\epsilon$ -nitro- $\gamma$ -ketohehoic acid with a solution of hydrogen bromide in glacial acetic acid at 100°, crystallises in colourless leaflets, m. p. 103°; the *methyl ester*,  $\text{C}_7\text{H}_9\text{O}_3\text{NBr}$ , forms colourless needles, m. p. 70—72°. The acid just described or the corresponding chloro-compound, when reduced with sodium amalgam in an alkaline aqueous solution, yields  *$\omega$ -cyanolævulinic acid*,  $\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , small, colourless crystals, m. p. 86—88°.

*3-Methoxyisooxazole-5-propionic acid*,  $\text{C}_7\text{H}_9\text{O}_4\text{N}$ , is formed when the corresponding halogen compound is boiled with a concentrated solution of potassium hydroxide in methyl alcohol; it crystallises in slender needles, m. p. 100°; the *methyl ester*,  $\text{C}_8\text{H}_{11}\text{O}_4\text{N}$ , has m. p. 56—57°. The acid is converted by hot concentrated nitric acid into a *nitro-derivative*,  $\text{C}_7\text{H}_8\text{O}_6\text{N}_2$ , which forms large, white crystals, m. p. 136—138°.

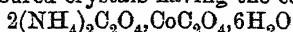
*isoOxazole-5-propionic acid*,  $\text{C}_6\text{H}_7\text{O}_3\text{N}$ , is prepared by treating the nitroketohehoic acid with tin and hydrochloric acid; it crystallises in white needles, m. p. 95—96°, and is converted by a methyl-alcoholic solution of potassium hydroxide into  *$\omega$ -cyanolævulinic acid*. W. H. G.

**Cobalto-oxalate-ammonia and Ammonium Cobalto-oxalate.** FRITZ EPHRAIM (*Ber.*, 1909, 42, 3850—3856).—When cobalt oxalate,  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , is dissolved in concentrated ammonia and the solution precipitated with alcohol, the compound  $\text{CoC}_2\text{O}_4 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$  is produced if care is taken to prevent oxidation. When quite dry it is reddish-violet in colour. The dry substance has an odour of ammonia, and on exposure to the air one molecule of ammonia is gradually replaced by water, with the formation of the compound  $\text{CoC}_2\text{O}_4 \cdot \text{NH}_3 \cdot 3\text{H}_2\text{O}$ . On the other hand, when exposed to an atmosphere of dry ammonia, the compound  $\text{CoC}_2\text{O}_4 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$  is produced. Anhydrous cobalt oxalate combines with ammonia, with the formation of the compound



Precipitated cobalt oxalate which has been dried at  $80^{\circ}$  contains  $2\text{H}_2\text{O}$ ; when the precipitation and drying take place at atmospheric temperature, the salt contains  $4\text{H}_2\text{O}$ .

Cobalt oxalate dissolves in a boiling mixture of one part of ammonium oxalate with five times its volume of water. If the cobalt oxalate is added only so long as it dissolves readily and the solution then filtered, rose-coloured crystals having the composition



are obtained on cooling. They are decomposed to some extent by water; the concentrated aqueous solution is deep violet in colour.

If an excess of cobalt oxalate is added to the solution of ammonium oxalate and the whole heated for some time in a reflux apparatus, a deep violet-coloured solution is obtained, which, on cooling, gives brown crystals having the composition  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{CoC}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$ . They are readily decomposed by water.

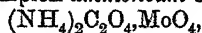
T. S. P.

**Complex Oxalates of Cobalt and Nickel.** STELLA DEAKIN, MARGARET SCOTT, and BERTRAM D. STEELE (*Zeitsch. physikal. Chem.*, 1909, 69, 123—135).—The nature of the complex oxalates present in solutions containing potassium oxalate and the oxalates of cobalt and nickel respectively has been established by solubility measurements at  $25^{\circ}$  and  $49^{\circ}$ . The respective oxalates of cobalt and nickel were shaken with solutions of potassium oxalate until equilibrium was established and the solutions analysed. The results accord best with the view that the solutions contain mainly the complexes  $(\text{K}_2\text{C}_2\text{O}_4)_2 \cdot (\text{CoC}_2\text{O}_4)_3$  and  $(\text{K}_2\text{C}_2\text{O}_4)_2 \cdot (\text{NiC}_2\text{O}_4)_3$ , but the solutions are in equilibrium with solid double salts of the respective formulæ  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{CoC}_2\text{O}_4$  and  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{NiC}_2\text{O}_4$ . The magnitude of the equilibrium constant increases with temperature in the case of cobalt and diminishes with temperature in the case of nickel. The interpretation of the results was complicated by the formation of solid solutions of potassium oxalate with both the other oxalates, and also by the occurrence of two equilibria in the nickel solutions, doubtless depending on the presence of two hydrates or other modifications of nickel oxalate.

From the results of electrical conductivity measurements, it is probable that the complex nickel salt is more highly ionised than potassium oxalate, but the velocity of the complex ion is much less than that of the oxalate ion.

G. S.

**Complex Acids of Molybdenum.** ARRIGO MAZZUCHELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 259—264).—Ammonium molybdo-oxalate, in presence of hydrogen peroxide, increases considerably in solubility, giving a bright yellow liquid, which deposits shining crystals of the complex ammonium compound,

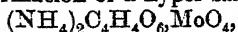


analogous in composition to the barium salt (*Abstr.*, 1907, i, 748). The corresponding potassium salt,  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{MoO}_4$ , forms lemon-yellow scales.

Unlike these salts, the acid molybdo-oxalates,  $\text{RHC}_2\text{O}_4 \cdot \text{MoO}_3$ , appear to alter in composition when hydrogen peroxide is added, the excess of oxalic acid being eliminated. Thus, the potassium salt, with 15% hydrogen peroxide solution, partly dissolves and then deposits yellow

crystals,  $K_2C_2O_4 \cdot 2MoO_4 \cdot 3H_2O$ . Also, the ammonium hydrogen salt dissolves readily in hydrogen peroxide solution, which deposits an orange-coloured powder,  $(NH_4)_2C_2O_4 \cdot 2MoO_4 \cdot 3H_2O$ , sparingly soluble in water, but hydrolysed by it with liberation of the active oxygen and oxalic acid; the sodium salt similarly gives  $Na_2C_2O_4 \cdot 2MoO_4$ .

From molybdotartrates, solid hyper-salts could not be isolated, owing to their great solubility and ready decomposability. A solution of  $(NH_4)_2C_4H_4O_6 \cdot MoO_3$  with an equivalent quantity of hydrogen peroxide becomes yellow, its molecular rotation, calculated on the tartaric acid (compare Rosenheim and Itzig, Abstr., 1900, i, 272), changing from  $+528^\circ$  to  $+203^\circ$ ; as the latter value is not altered by addition of a triple proportion of hydrogen peroxide, the change in rotation is due to the formation of a hyper-salt, evidently



and not to decomposition of the original compound into ammonium permolybdate and tartrate. The rotations of solutions of tartaric acid containing increasing proportions of yellow molybdic acid and hydrogen peroxide increase from  $+183^\circ$  to  $+428^\circ$  for  $4MoO_4$  per  $C_4H_4O_6$ , after which further addition of molybdic acid causes no further increase in rotation. Similarly, the rotation of sodium molybdomalate changes from  $+134^\circ$  to the constant value,  $-140^\circ$ , on addition of hydrogen peroxide; in this case, the catalytic decomposition of the hydrogen peroxide is far more rapid than with the tartrate, and, ultimately, the rotation assumes a value,  $+150^\circ$ , nearly equal to the original value.

Cryoscopic measurements with ammonium molybdo-oxalate show that the number of molecules remains practically unchanged by addition of hydrogen peroxide, not only in the proportion of 1 mol. to 1 mol. (corresponding with the solid hyper-salt obtained), but almost up to the proportion of 2 mols.  $H_2O_2$  to 1 mol. of molybdo-oxalate. That a partial scission into ammonium oxalate and permolybdate is here caused by the excess of hydrogen peroxide is confirmed by the cryoscopic results obtained with ammonium hydrogen molybdo-oxalate.

The cryoscopic data for molybdo-iodic acid do not show, with certainty, the existence of a hyper-acid, but indicate that the molybdo-iodic acid undergoes polymerisation.

A higher degree of polymerisation is found for yellow molybdic acid than was obtained by Rosenheim and Bertheim (Abstr., 1903, ii, 374), and cryoscopic measurements of solutions of molybdic acid containing hydrogen peroxide indicate that the per-acid,  $MoO_3 \cdot H_2O_2$ , also undergoes polymerisation, thus explaining the possibility of adding  $4MoO_4$  to the tartrate (*vide supra*). With the molybdic acid obtainable from methyl molybdate,  $Me_3MoO_4$ , which acid Rosenheim and Davidsohn (Abstr., 1904, ii, 128) assert consists of a simple molecule, results are obtained similar to those given by yellow molybdic acid.

The number of molecules in solutions containing either the molybdic acid obtained from methyl molybdate or the yellow acid, together with various proportions of sulphuric acid, indicate that a compound between  $SO_3$  and  $MoO_3$  persists in these solutions. T. H. P.

**Aliphatic Compounds of Polyvalent Iodine. I. Iodo-chlorides and Iodoso-compounds from Chloriodofumaric Acid.** JOHANNES THIELE and WILLI PETER (*Annalen*, 1909, 369, 119—128).—An account of this work has already appeared (compare *Abstr.*, 1905, i, 735). The following compounds have not been described hitherto.

*Methyl iodofumarate*,  $C_6H_7O_4I$ , crystallises in yellow prisms, m. p. 52—52.5°. Neither this substance nor the acid itself yields an iodochloride when the solution in chloroform is treated with chlorine at 0°.

*Iodomaleic acid*,  $C_4H_3O_4I$ , is obtained by heating iodofumaric acid with phosphoryl chloride on a water-bath; it crystallises in almost colourless prisms, m. p. 153—154°.

*Chloriodosuccinic acid*,  $CO_2H \cdot CHI \cdot CHCl \cdot CO_2H$ , formed by the action of chlorine iodide on maleic acid in ethereal solution, crystallises in colourless spangles, m. p. 164—166°. Although chloriodosoacrylic acid is stable at the ordinary temperature, it is not possible to prepare in the same way an iodosochloride of chloriodosuccinic acid, showing that the stability of the former compound is due to the union of iodine with an ethenoid carbon atom.

The compound described previously (*loc. cit.*) as an acetyl derivative of chloriodofumaric acid iodosochloride is now shown to be the iodosochloride of chloroacrylic acid.

W. H. G.

**Aliphatic Compounds of Polyvalent Iodine. II. Derivatives of Di-iodofumaric Acid with Polyvalent Iodine.** WILLI PETER (*Annalen*, 1909, 369, 128—130. Compare preceding abstract).—Di-iodofumaric acid in aqueous solution is converted by chlorine

into the *iodosochloride* of iodofumaric acid,  $O \begin{smallmatrix} \text{CO} - \text{Cl} \\ | \\ \text{I} \cdot \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$ , which crystallises in small, greenish-yellow needles, decomposes at 117°, and when treated with hot water loses carbon dioxide, yielding *iodiodosoacrylic acid*,  $O \begin{smallmatrix} \text{CO} - \text{Cl} \\ | \\ \text{I}(\text{OH}) \cdot \text{CH} \end{smallmatrix}$ , small, colourless crystals, m. p. 169—170°.

The latter substance is reduced by sulphurous acid, yielding  $\alpha\beta$ -di-iodoacrylic acid.

It is remarkable that only one of the iodine atoms of di-iodofumaric acid combines with chlorine (compare this vol., i, 865).

W. H. G.

**Preparation of Iron Hydrogen Phosphotartrates and Phosphocitrates.** CARL SORGER (D.R.-P. 211529 and 211530).—*Ferrous hydrogen phosphotartrate* is prepared by stirring tartaric acid into a suspension of ferrous phosphate in water until a solution is obtained. After several days the colourless, crystalline precipitate is collected, and dried at a low temperature in the dark.

*Ferric hydrogen phosphotartrate* slowly separates as a greenish-yellow powder when a solution of ferric tartrate is treated with phosphoric acid. These compounds, which are tasteless, odourless, and sparingly soluble in water or dilute acids, but readily so in ammonium hydroxide and alkalis, are of therapeutic value.

*Ferrous hydrogen phosphocitrate*, a greyish-white powder, is prepared by adding citric acid to a suspension of ferrous phosphate.

*Ferric hydrogen phosphocitrate* is formed (1) when citric acid is added to ferric phosphate (2) by treating a solution of ferric citrate with phosphoric acid. These salts are more readily soluble in water and dilute acids than the corresponding phosphotartrates. F. M. G. M.

**Preparation of Alkyl Methylenecitrates.** FARBENFABRIKEN VORM F. BAYER & Co. (D.R.-P. 212554).—*Diethyl methylenecitrate* is prepared by heating together methylenecitric acid, alcohol, and sulphuric acid; it crystallises as tasteless, odourless tablets, m. p. 55°.

*Amyl methylenecitrate* is prepared by heating the acid chloride with amyl alcohol in benzene solution in the presence of pyridine. It has similar properties, and crystallises in scales, m. p. 52—55°.

F. M. G. M.

**Nitroacetaldehydediethylacetal.** MILIVOJ S. LOSANITSCH (*Ber.*, 1909, 42, 4044—4049. Compare Meister, *Abstr.*, 1907, i, 886).— $\beta$ -Nitroacetaldehydediethylacetal,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , can be prepared by heating  $\beta$ -iodoacetaldehydediethylacetal (Hesse, *Abstr.*, 1897, i, 457) with silver nitrite during three days. It has b. p. 89—91°/14 mm., forms a clear, colourless liquid heavier than water, and has a faint odour. It gives V. Meyer's nitroso-reaction feebly, yields sodium derivatives, and can be reduced by sodium and boiling alcohol to the amino-acetal (Wohl), b. p. 78—80°/15 mm.

When mixed with concentrated hydrochloric acid, and subsequently treated with phenylhydrazine acetate, the nitro-compound yields glyoxalosazone.

J. J. S.

**Preparation of Disulphoacetaldehydesulphoxylates.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 212070).—*Sodium disulphoacetaldehydesulphoxylate*,  $(\text{SO}_3\text{Na})_2\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{SO}_3\text{Na}$ , is prepared by treating sodium acetaldehydedisulphonate,  $\text{CH}(\text{SO}_3\text{Na})_2\cdot\text{CHO}$ , with zinc dust and a current of sulphur dioxide; the solution of the sodium salt is evaporated at a low temperature in a vacuum and treated with alcohol. The salts of this acid are odourless and of therapeutic value. The corresponding formaldehyde compound was not obtained in a pure state.

F. M. G. M.

**Ketens. XII. Preparation of Keten.** HERMANN STAUDINGER and J. KUBINSKY (*Ber.*, 1909, 42, 4213—4215).—It was shown by Staudinger and Klever (*Abstr.*, 1908, i, 246) that keten may be prepared by treating bromoacetyl bromide in ether or ethyl acetate with zinc, but that no keten is obtained in this way from chloroacetyl chloride. The authors have now carried out further experiments with (1) bromoacetyl bromide, which yielded from 7 to 13% of keten; (2) bromoacetyl chloride, which gave 3—4% of keten; (3) chloroacetyl bromide, and (4) chloroacetyl chloride, neither of which yielded keten, the conditions being the same in each case. If, therefore, for the preparation of a new keten the  $\alpha$ -brominated acid bromide is not available, it is better to employ the  $\alpha$ -brominated acid chloride rather

than the  $\alpha$ -chlorinated acid bromide, since it is the chlorine atom of the  $\text{CH}_2\text{Cl}$  group which is so strongly combined that it is not attacked. The fact that diphenylchloroacetyl chloride readily enters into reaction under conditions where chloroacetyl chloride is not attacked is explained by the loosening of the chlorine atom by the two phenyl groups; the same reason applies to the relatively great reactivity of diphenyl- and triphenyl-chloromethane compared with chloromethane itself.

Bromoacetyl bromide is attacked readily by magnesium, giving a large yield of keten, but at the end of the reaction such large quantities of hydrogen bromide are formed that no keten can be isolated; the action of silver is slight, whilst with potassium, sodium, calcium, iron, aluminium, and cadmium, no action is observed.

T. H. P.

**Sugar Scissions. VI. The Electrolytic Reduction of Dextrose.** WALTHER LÖB (*Biochem. Zeitsch.*, 1909, 21, 102—105).—It has already been shown (Abstr., 1909, i, 767) that dextrose can give rise to pentose and formaldehyde when submitted to electrolysis at the lead anode. The same products can also be detected when the sugar solution is electrolysed at a lead cathode.

S. B. S.

**Action of Fehling's Solution on Galactose.** ERNEST ANDERSON (*Amer. Chem. J.*, 1909, 42, 401—431).—Nef (Abstr., 1908, i, 7) has shown that when dextrose,  $d$ -mannose, and lævulose are oxidised with Fehling's solution, the products consist of carbonic, formic, oxalic, glycollic,  $d$ - and  $l$ -glyceric,  $l$ -threonic,  $d$ -erythronic, and isomeric hexonic acids. A study has now been made of the oxidation of galactose, and it has been found that, whilst the members of the dextrose series yield a large amount of  $d$ -gluconic acid, smaller quantities of  $d$ -mannonic acid, and probably some  $\alpha$ -hydroxymethyl- $d$ -arabonic acid,  $d$ -galactose gives much  $d$ -galactonic acid, relatively smaller amounts of  $d$ -talonic acid, and probably small quantities of  $\alpha$ -hydroxymethyl- $d$ -lyxonic acid. The mechanism of the oxidation is discussed.

The oxidation of 118 grams of  $d$ -galactose yielded 2.49 grams of carbon dioxide, 15.69 grams of formic acid, and 102.1 grams of non-volatile acids. From the last-mentioned were isolated 13 grams of  $d$ -galactonic acid, 5.33 grams of  $d$ -talonic acid, 0.5 gram of oxalic acid, 2.58 grams of  $l$ -threonic lactone, traces of  $d$ -erythronic lactone, about 11 grams of  $dl$ -glyceric acid, and 11.75 grams of glycollic acid. It is estimated that the 102 grams of non-volatile acids actually contained 20—30 grams of glycollic acid, 20—30 grams of glyceric acid, 4—8 grams of trihydroxybutyrolactones, and 20—30 grams of hexonic acids.

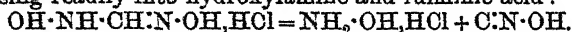
E. G.

**Lactic Acid in Alcoholic Sucrose Fermentation.** EDUARD BUCHNER and JAKOB MEISENHEIMER (*Landw. Jahrb.*, 1909, 38, v, 265—288. Compare Abstr., 1904, ii, 199; 1905, ii, 274; 1906, i, 919, ii, 790).—A detailed account of experiments leading to the conclusion that lactic acid is not formed as a by-product during the cell-free alcoholic fermentation of sucrose.

F. M. G. M.

**Action of Calcium Hydroxide on Lactose.** HEINRICH KILIANI (*Ber.*, 1909, 42, 3903—3904).—By the action of calcium hydroxide on lactose a mixture of the three saccharinic acids is obtained. An alteration in the method of procedure enables these substances to be relatively easily prepared. A solution of one part of milk sugar in nine parts of water with 0.2 part of calcium hydroxide is shaken in a closed flask for two days and then heated for ten hours in a boiling water-bath. The dark red filtrate is separated from a precipitate, mostly consisting of calcium carbonate, and concentrated, whereby calcium isosaccharinate separates. The mother liquors are freed from calcium, evaporated to a syrup, extracted with ether, and the residue converted into a barium salt, which is induced to crystallise in the usual manner; it consists of meta- and para-saccharinate. Since the constitution of the saccharins has been determined, it is advisable to use their correct names: isosaccharinic acid is  $\alpha\gamma\delta$ -triol- $\alpha$ -methylpentoic acid, metasaccharinic acid is  $\alpha\gamma\delta$ -tetrolhexoic acid, para-saccharinic acid is  $\alpha\beta\gamma$ -triol- $\alpha$ -ethanolbutyric acid, whilst Peligot's saccharinic acid is tetrol- $\alpha$ -methylpentoic acid. E. F. A.

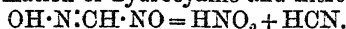
**Methylnitrosolic Acid and Allied Compounds.** HEINRICH WIELAND and HERMANN HESS (*Ber.*, 1909, 42, 4175—4191).—It was shown by Nef (*Abstr.*, 1895, i, 9) that when an alcoholic solution of formamino-oxime is heated with hydroxylamine hydrochloride, ammonium chloride is deposited and a new compound, hydroxyisouretin, formed. The authors find that the latter is, in reality, formhydroxylamino-oxime,  $\text{OH}\cdot\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ , which could not be isolated even in the form of hydrochloride, the latter decomposing readily into hydroxylamine and fulminic acid:



The base gives with ferric chloride the dark blue coloration characteristic of the hydroxylamino-oximes, reduces silver nitrate immediately, and yields a red coloration with sodium hydroxide.

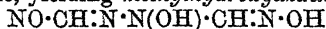
*Potassium methylnitrosolate*,  $\text{OK}\cdot\text{N}\cdot\text{CH}\cdot\text{NO}$ , prepared by the action of alcoholic potassium hydroxide on formhydroxylamino-oxime, forms shining, indigo-blue prisms, exploding at  $194^\circ$ , or when subjected to shock. The aqueous solution exhibits no selective absorption, the spectrum being continuous from the red to between the yellow and green. The silver salt was analysed, and the copper, lead, nickel, mercuric, and mercurous salts prepared. Free methylnitrosolic acid, the formation of which from formhydroxylamino-oxime is represented by the scheme:  $2\text{OH}\cdot\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH} \rightarrow \text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{N}\cdot\text{CH}\cdot\text{N}\cdot\text{OH} \rightarrow \text{NH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{OH} + \text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{NO}$ , separates in the bimolecular form:  $\text{OH}\cdot\text{N}\cdot\text{CH}\cdot[\text{NO}]_2\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$  (?), exploding at  $76^\circ$ . Secondary nitroso-compounds containing the group  $\cdot\text{CH}\cdot\text{NO}$ , as a rule, readily undergo enolisation, giving the oxime,  $\cdot\text{C}\cdot\text{N}\cdot\text{OH}$ , but the bimolecular form of methylnitrosolic acid never yields the dioxime of carbon dioxide,  $\text{OH}\cdot\text{N}\cdot\text{C}\cdot\text{N}\cdot\text{OH}$ , but always the primary salts of the monobasic methylnitrosolic acid, owing probably to the disinclination of the carbon atom to combine with two groups by two double linkings. The salts of methylnitrosolic acid, under the prolonged action of alkali,

decompose with formation of hydrocyanic and nitrous acids :

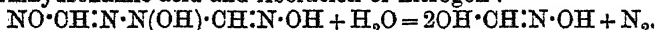


The free acid decomposes extremely readily, mostly into hyponitrous acid and fulminic acid:  $2\text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{NO} = \text{OH}\cdot\text{N}\cdot\text{N}\cdot\text{OH} + (\text{C}\cdot\text{N}\cdot\text{OH})_2$  (compare Abstr., 1907, i, 196; this vol., i, 215).

When the action of alkali hydroxide on formhydroxylamino-oxime takes place at low temperatures, no salt of nitrosolic acid is obtained, since, as this acid is formed, it condenses with the excess of formhydroxylamino-oxime, yielding *methylhydroxyazaurolic acid*,



(compare Abstr., 1907, i, 494), in the form of straw-yellow needles exploding at  $103^\circ$ . This acid explodes with a flash when treated with a concentrated mineral acid; with acidified potassium iodide solution it gives a precipitate of iodine, and with ferric chloride a dark orange-red coloration gradually appears; it gives Liebermann's reaction with phenol and sulphuric acid, and its scarlet *silver* salt is decomposed by nitric acid, yielding silver cyanide. The *copper* and *potassium* salts,  $\text{C}_2\text{H}_2\text{O}_5\text{N}_4\text{K}_2$ , were prepared, and also the *benzoyl* derivative, m. p.  $141^\circ$  (decomp.). Its reactions resemble closely those of hydroxyethylazaurolic acid, but it does not undergo transformation into hydroxy-leucazone with loss of nitrous oxide. When gently heated with water, it decomposes partly into nitrogen, carbon dioxide, and hydrogen cyanide, and partly into nitrogen, water, and isocyanic acid (or carbon dioxide and ammonia):  $\text{C}_2\text{H}_2\text{O}_5\text{N}_4 = \text{N}_2 + 2\text{HCON} + \text{H}_2\text{O}$ ; in the latter case a residue remains consisting apparently of a new acid and its ammonium salt, which were not investigated. By the action of concentrated hydrochloric acid in the cold, it is decomposed with formation of formhydroxamic acid and liberation of nitrogen:



The reduction of methylhydroxyazaurolic acid to methylazaurolic acid does not proceed so readily as with other hydroxyazaurolic acids. But methylazaurolic acid can be obtained by reducing the hydroxy-acid by hydrogen sulphide to hydrazoformoxime and oxidising the latter by means of bromine vapour.

*Hydrazoformoxime*,  $\text{OH}\cdot\text{N}\cdot\text{CH}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ , also prepared by the action of hydrazine hydrochloride on formamino-oxime, forms thin, colourless prisms, decomp. at  $138-140^\circ$ . With ferric chloride, it gives a green coloration, changing to brown, and its *picrate* forms golden-yellow needles, m. p.  $226^\circ$ .

*Methylazaurolic acid*,  $\text{NO}\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$ , forms long, dark yellow prisms, m. p.  $138^\circ$  (detonat.). The *sodium*, *barium*, *silver*, and *copper* salts, which are all explosive, were prepared. The acid is less readily decomposed than the corresponding hydroxy-acid, and, on boiling with water, it yields gaseous products and 80—90% of an orange-red, amorphous acid. When treated in the cold with concentrated hydrochloric acid, it undergoes isomeric change, yielding *isozaurolin* (isonitrosodihydro-oxotriazine),  $\text{CH}\langle\begin{smallmatrix} \text{N} & \text{O} \\ \text{NH} & \text{NH} \end{smallmatrix}\rangle\text{C}\cdot\text{N}\cdot\text{OH}$ ,

which forms colourless needles, becoming orange-yellow at about  $85^\circ$  and exploding at  $112-113^\circ$ . This base undergoes oxidation in the air to a red azo-compound, but it is not attacked by concentrated

hydrochloric acid even at  $140^{\circ}$ . Its *hydrochloride*,  $C_2H_4O_2N_4 \cdot HCl$ , decomposes at  $148-150^{\circ}$ .

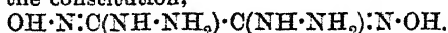
*Formoximehydrazocarbonamide*,  $OH \cdot N : CH \cdot NH \cdot NH \cdot CO \cdot NH_2$ , prepared by the action of semicarbazide on formamino-oxime, forms colourless needles, decomposing at  $154^{\circ}$ . It reduces ammoniacal silver solutions instantaneously, and, with ferric chloride, gives a dark blue coloration, rapidly changing to green.

*Formoximeazocarbonamide*,  $OH \cdot N : CH \cdot N : N \cdot CO \cdot NH_2$ , prepared by oxidising formoximehydrazocarbonamide by means of bromine vapour, was obtained in impure, orange-red, stellate aggregates of broad needles, decomposing at  $123-126^{\circ}$  or  $138^{\circ}$ . It gives Liebermann's reaction with phenol and sulphuric acid, and, when it is heated with ferric chloride, hydrogen cyanide is evolved, and an intense, greenish-brown coloration formed. When heated in alkali solution, it decomposes according to the equation:  $OH \cdot N : CH \cdot N : N \cdot CO \cdot NH_2 = HCN + N_2 + CO_2 + NH_3$ . The *silver* salt and the soluble *barium* and *lead* salts were prepared.

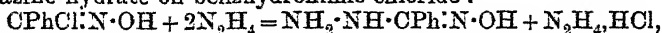
Phenylhydrazoformaldoxime, obtained by Bamberger and Frei (Abstr., 1902, i, 404) by the action of hydrogen sulphide on  $\alpha$ -nitroformaldehydephenylhydrazone, is also formed by the action of phenylhydrazine on formamino-oxime.

T. H. P.

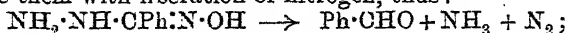
**Hydrazide-oximes.** HEINRICH WIELAND (*Ber.*, 1909, 42, 4199-4206).—The action of the hydrazine hydrate on dibromofuroxan yields the hydrazine analogue of oxamidedioxime (compare this vol., i, 892) having the constitution,



To the compounds of this type the author gives the name *hydrazide-oximes*. The reactions of benzhydrazide-oxime, prepared by the action of hydrazine hydrate on benzhydroximic chloride:



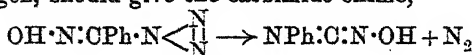
have been investigated. The hydrazide-oximes possess an amphoteric character and, like the amino-oximes, dissolve in both mineral acids and alkalis. Towards acids they are moderately stable, but alkalis readily decompose them with liberation of nitrogen, thus:



the benzaldehyde then condenses with unchanged hydrazide-oxime, giving, as final product, the stable benzylidenebenzhydrazide-oxime,  $CHPh : N \cdot NH \cdot CPh : N \cdot OH$ , which, in contact with acids, readily

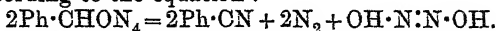
undergoes transformation into diphenyltriazole,  $CPh \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CPh}$  (compare Pinner, Abstr., 1897, i, 637).

Assuming that the hydrazine residue of the hydrazide-oximes reacts with nitrous acid in the same way as does that of the acid hydrazides, benzhydrazide-oxime should yield benzhydroximic azoimide, which, by loss of nitrogen, should give the carbimide oxime,



(compare Forster, Trans., 1909, 95, 184). But this is not actually the case, the reaction between benzhydrazide-oxime and nitrous acid

yielding the 1-hydroxy-5-phenyltetrazole obtained by Forster by the interaction of benzhydroxamic chloride and sodium azoimide (*loc. cit.*). The decomposition of 1-hydroxy-5-phenyltetrazole by dilute alkali proceeds according to the equation :



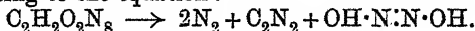
A similar decomposition is exhibited by the dihydroxybistetrazyl obtained by the action of nitrous acid on oxaldihydrazide-oxime.

*Benzhydrazide-oxime*,  $\text{OH}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{NH}_2$ , forms snow-white needles, decomp. at  $110^\circ$ , and is stable in a desiccator or in the air, but decomposes rapidly in a closed vessel. It reduces Fehling's solution and ammoniacal silver solutions instantaneously, and with ferric chloride gives an intense, cherry-red coloration. Its *hydrochloride* forms stellate aggregates of needles.

*Benzylidenebenzhydrazide-oxime*,  $\text{OH}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$ , forms fan-shaped aggregates of white, silky needles, m.p.  $120^\circ$  (decomp.), and with ferric chloride gives a blue coloration, rapidly changing to green.

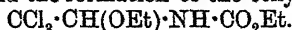
*Oxaldihydrazide-oxime*,  $\text{OH}\cdot\text{N}:\text{C}(\text{NH}\cdot\text{NH}_2)\cdot\text{C}(\text{NH}\cdot\text{NH}_2):\text{N}\cdot\text{OH}$ , formed by the interaction of dibromofuroxan and hydrazine hydrate, is extremely soluble in water and decomposes very readily, so that it could be obtained only as its *hydrazine* salt,  $\text{C}_2\text{H}_5\text{O}_2\text{N}_6\cdot\text{N}_2\text{H}_4$ , in colourless leaflets, which explode violently in a melting-point tube at  $108^\circ$ . The salt is stable in an open vessel in the dark, but is decomposed readily by hydrochloric acid, giving nitrogen and hydrocyanic and oxalic acids. With ferric chloride it yields a dark blue coloration, which is not affected by acids. With benzaldehyde it forms benzalazine and colourless *benzylideneoxaldihydrazide-oxime*, which was not obtained pure and which gives a brownish-green coloration with ferric chloride.

*Dihydroxybistetrazyl*,  $\begin{array}{c} \text{N} \cdot \text{N}(\text{OH}) \\ \parallel \quad \diagup \\ \text{N} \text{---} \text{N} = \text{C} \cdot \text{C} = \text{N}(\text{OH}) \cdot \text{N} \\ \parallel \quad \diagdown \\ \text{N} \text{---} \text{N} \end{array}$ , forms broad, colourless needles, exploding violently when subjected to friction or a blow, or when heated to 176° in a melting-point tube. It gives a brownish-red coloration with ferric chloride, and is decomposed by alkalis according to the equation :



T. H. P.

**Chloralurethane.** OTTO DIELS and CARL SEIB (*Ber.*, 1909, 42, 4062—4072. Compare Bischoff, *Ber.*, 1874, 7, 631; Moscheles, *Abstr.*, 1891, 1003).—According to Hantzsch (*Abstr.*, 1894, i, 363), anhydrochloralurethane reacts with sodium ethoxide, yielding hydrogen chloride and dichloroethyleneurethane,  $\text{CCl}_3\cdot\text{CH:N}\cdot\text{CO}_2\text{Et} = \text{HCl} + \text{CCl}_2\text{:C:N}\cdot\text{CO}_2\text{Et}$ , but, according to the authors, the reaction consists in the addition of ethyl alcohol to the double linking in the anhydro-compound and the formation of the ethyl ether,



Methyl alcohol unites itself in a similar manner, and additive compounds with urethane or ethyl malonate can also be obtained, namely, chloraldiurethane and  $\text{CCl}_3 \cdot \text{CH}(\text{NH} \cdot \text{CO}_2\text{Et}) \cdot \text{CH}(\text{CO}_2\text{Et})_2$  respectively.

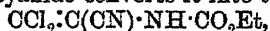
*Chloralurethane ethyl ether*,  $\text{CCl}_3\cdot\text{CH}(\text{OEt})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , has an odour of cloves, distils at  $134^\circ/13\text{ mm.}$ , and solidifies to crystalline rosettes, m. p.  $37^\circ$ . With concentrated sulphuric acid it yields chloral. The corresponding *methyl ether*,  $\text{C}_6\text{H}_{10}\text{O}_3\text{NCl}_3$ , has b. p.  $137^\circ/22\text{ mm.}$ , and m. p.  $64^\circ$ .

*Chloraldiurethane*,  $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})_2$ , obtained by the action of sodium urethane on an ethereal solution of anhydrochloralurethane and treatment of the product with dilute hydrochloric acid, crystallises from acetone in well-developed needles, m. p.  $172^\circ$ . The same product is formed by the prolonged action of chlorine on urethane in the presence of a little iodine, or by the action of a few drops of concentrated sulphuric acid on a mixture of chloral (5 parts) and urethane (6 parts).

The compound,  $\text{CCl}_3\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , distils at  $198\text{--}199^\circ/12\text{ mm.}$ , and  $\gamma$ -trichloro- $\beta$ -aminopropionic acid,  $\text{CCl}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,

obtained by hydrolysing at  $95\text{--}100^\circ$  the above compound with a glacial acetic acid solution of hydrogen bromide (saturated at  $0^\circ$ ), crystallises from ethyl acetate in colourless prisms, m. p.  $189^\circ$  (decomp.).

The *acetyl* derivative of chloralurethane,  $\text{CCl}_3\cdot\text{CH}(\text{OAc})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , prepared by the action of acetyl chloride on the urethane, is a viscid, strongly refractive liquid, b. p.  $165^\circ/15\text{ mm.}$  It solidifies slowly, and has m. p.  $47\text{--}49^\circ$ . Hydrolysing agents convert it into anhydrochloralurethane, and boiling for some time with a saturated aqueous solution of potassium cyanide converts it into the *nitrile*,



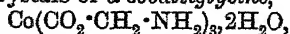
which crystallises from dilute alcohol in colourless, felted needles, m. p.  $113\text{--}114^\circ$ .

When hydrolysed in sealed tubes with an acetic acid solution of hydrogen bromide at  $0^\circ$ , the nitrile yields ethyl bromide and  $\beta$ -dichloro- $\alpha$ -aminoacrylic acid?,  $\text{CCl}_2\cdot\text{C}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ , m. p.  $113^\circ$  after sintering at  $80^\circ$ .

J. J. S.

**Stereoisomerism of Internally Complex Salts.** HEINRICH LEY and H. WINKLER (*Ber.*, 1909, 42, 3894—3902).—Cobaltiglycine,  $\text{Co}(\text{CO}_2\cdot\text{CH}_2\cdot\text{NH}_2)_3$ , a typical internal complex salt, is found to exist in two modifications, which must be stereoisomeric, as the chemical behaviour of both is almost the same, and a difference of molecular weight does not exist. Two configurations are possible for the cobaltic compound, namely, a *bis-cis* and a *trans-cis* configuration, using Werner's octahedral scheme. It is not yet possible to determine the modification to which each configuration corresponds.

Air oxidises a mixture of glycine with a cobaltous salt, but mixtures of different cobaltic salts are obtained. A solution of glycine in water is boiled for five hours with an excess of cobaltic hydroxide. The filtered red solution, when concentrated on the water-bath, deposits dark violet crystals of  $\alpha$ -cobaltiglycine,



which separates from hot water in large, rhombic, pleochroic crystals.

The solution in sulphuric acid has two absorption bands, at  $1/\lambda$  2000 and 2800 respectively.

$\beta$ -Cobaltglycine,  $\text{Co}(\text{CO}_2\cdot\text{CH}_2\cdot\text{NH}_2)_3\cdot\text{H}_2\text{O}$ , is obtained as an insoluble residue in the above preparation, and, after washing with hot water, forms minute, pale red needles. The position of the absorption bands in sulphuric acid solution is only slightly different from the  $\alpha$ -form. The difference of water of crystallisation does not account for the difference of properties, as the colours are little altered by dehydration. The  $\beta$ -modification reacts readily with potassium nitrite to form a complex salt, the  $\alpha$ -form only with great difficulty.

Other properties of the salts are under investigation. C. H. D.

**Synthesis of Polypeptides. XXXI. Derivatives of Leucine, Alanine, and *N*-Phenylglycine.** EMIL FISCHER and WILHELM GLUUD (*Annalen*, 1909, 369, 247—275. Compare this vol., i, 367).—With the object of gaining some knowledge of the properties of methylated polypeptides, the two dipeptides, *N*-methyl-leucylglycine and *N*-dimethyl-leucylglycine, have been prepared by the action of methylamine and dimethylamine on inactive  $\alpha$ -bromoisohexoylglycine. The first named is very similar to leucylglycine, both in its physical and chemical properties; thus, when heated, it passes into an anhydride. The dimethyl compound, from the nature of its constitution, cannot behave in the same way; when heated, it decomposes in a very complex manner.  $\alpha$ -Bromoisohexoylglycine, when heated with trimethylamine at  $100^\circ$ , yields  $\alpha$ -hydroxyisohexoylglycine; the same compound is formed when an aqueous solution of pyridine is used instead of trimethylamine.

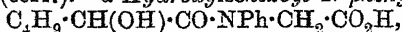
$\alpha$ -Bromoisohexoyl-*N*-phenylglycine, when treated with ammonia, behaves like  $\alpha$ -bromoisohexoylproline, in that it yields  $\alpha$ -hydroxyisohexoyl-*N*-phenylglycinamide instead of a dipeptide (compare Fischer and Reif, *Abstr.*, 1908, i, 1007);  $\alpha$ -bromopropionyl-*N*-phenylglycine undergoes a similar change when acted on by ammonia, whilst chloroacetyl- and bromoacetyl-*N*-phenylglycine do not yield hydroxyacetyl-*N*-phenylglycinamide as anticipated, but a substance which is probably a diketopiperazine-like anhydride of iminodiacetyl-*N*-phenylglycine,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CO} \\ \text{CO}\cdot\text{CH}_2\end{smallmatrix}\rangle\text{NPh}$ . Glycyl-*N*-phenylglycine is formed together with the latter substance by the action of ammonium hydroxide on chloroacetyl-*N*-phenylglycine at the ordinary temperature (compare Leuchs and Manasse, *Abstr.*, 1907, i, 770).

dl-*N*-Methyl-leucylglycine,  $\text{C}_4\text{H}_9\cdot\text{CH}(\text{NHMe})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises in short, compact prisms and small, almost rectangular plates, m. p.  $225^\circ$  (decomp., corr.); the anhydride,  $\text{C}_9\text{H}_{16}\text{O}_3\text{N}_2$ , crystallises in small, colourless, rhombic plates, m. p.  $114^\circ$  (corr.).

dl-*N*-Dimethyl-leucylglycine,  $\text{C}_4\text{H}_9\cdot\text{CH}(\text{NMe}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises with  $1\frac{1}{2}\text{H}_2\text{O}$  in slender prisms and small, rectangular plates, m. p.  $97^\circ$  (corr.); the anhydrous substance has m. p.  $160^\circ$ , and decomposes at  $220^\circ$  with the elimination of water and dimethylamine; the copper salt,  $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_2\text{Cu}$ , crystallises with  $\text{H}_2\text{O}$  in small, hexagonal, and rhombic plates.

$\alpha$ -Bromoisohexoyl-*N*-phenylglycine,  $\text{C}_4\text{H}_9\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,

is most readily obtained through the methyl ester by the interaction of *N*-phenylglycine methyl ester and  $\alpha$ -bromoisohexoyl bromide in chloroform at about  $-10^{\circ}$ ; it crystallises with  $1\text{H}_2\text{O}$  in colourless, nearly rectangular plates, m. p.  $66^{\circ}$  (corr.).  *$\alpha$ -Hydroxyisohexoyl-N-phenylglycinamide*,  $\text{C}_4\text{H}_9\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ , forms tufts of colourless plates, which lose 10—12% of their weight (benzene?) when kept in a vacuum desiccator; the substance, dried at  $100^{\circ}$ , has m. p.  $128\text{--}129^{\circ}$  (corr.).



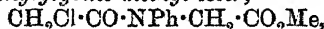
prepared by heating the substance just described with a 5-*N*-hydrochloric acid solution or by acting on the corresponding bromo-compound with sodium hydroxide, crystallises in microscopic, hexagonal, or rhombic plates, m. p.  $129\text{--}130^{\circ}$  (corr.), at which temperature it yields the anhydride,  $\text{C}_{14}\text{H}_{17}\text{O}_3\text{N}$ , microscopic plates and prisms, m. p.  $75\text{--}76^{\circ}$ .

*$\alpha$ -Bromopropionyl-N-phenylglycine methyl ester*,  $\text{C}_{12}\text{H}_{14}\text{O}_3\text{NBr}$ , prepared from  $\alpha$ -bromopropionyl bromide and *N*-phenylglycine methyl ester, crystallises in large, rectangular plates, m. p.  $78\text{--}79^{\circ}$  (corr.);  *$\alpha$ -bromopropionyl-N-phenylglycine*,  $\text{CHMeBr}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , crystallises with  $1\text{H}_2\text{O}$  in stellate aggregates of slender, colourless needles, m. p.  $79\text{--}80^{\circ}$  (corr.).



prepared by the action of a methyl-alcoholic solution of ammonia on the substance just described, forms stellate aggregates of colourless, slender prisms, m. p.  $125^{\circ}$  (corr.); it is also produced together with ammonium lactyl-N-phenylglycine,  $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{NH}_4$ , crystallising in tufts of microscopic, colourless plates and prisms, m. p.  $159^{\circ}$  (decomp., corr.), when aqueous ammonia is employed.

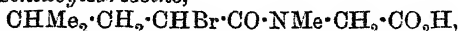
*Chloroacetyl-N-phenylglycine methyl ester*,



prepared from chloroacetyl chloride and *N*-phenylglycine methyl ester, crystallises in pointed prisms, m. p.  $59\text{--}60^{\circ}$  (corr.); the corresponding bromo-compound,  $\text{C}_{11}\text{H}_{12}\text{O}_3\text{NBr}$ , crystallises in thin leaflets, m. p.  $71^{\circ}$  (corr.).

*Iminodiacetyl-N-phenylglycine anhydride*,  $\text{C}_{20}\text{H}_{19}\text{O}_5\text{N}_3$ , crystallises with  $\frac{1}{2}\text{H}_2\text{O}(\text{?})$  in long, pointed needles and compact prisms; the anhydrous substance has m. p.  $226^{\circ}$  (decomp., corr.); the copper salt,  $\text{C}_{40}\text{H}_{36}\text{O}_{10}\text{N}_6\text{Cu}$ , crystallises with  $\text{H}_2\text{O}$  in microscopic, bluish-green needles and short prisms; the anhydrous salt is hygroscopic and decomposes just above  $200^{\circ}$ .

*dl- $\alpha$ -Bromoisohexoylsarcosine*,

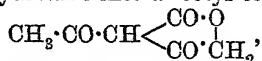


prepared by the action of *dl- $\alpha$* -bromoisohexoyl bromide on sarcosine in the presence of sodium hydroxide, crystallises in colourless needles and prisms, m. p. about  $90^{\circ}$ .

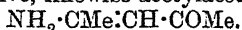
*$\alpha$ -Hydroxyisohexoyl-glycine*,  $\text{C}_4\text{H}_9\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , has m. p.  $109^{\circ}$  (corr.); the copper salt,  $\text{C}_{16}\text{H}_{28}\text{O}_8\text{N}_2\text{Cu}\cdot 2\text{H}_2\text{O}$ , forms stellate aggregates of microscopic, pale blue needles. W. H. G.

**Acylation of Ethyl  $\beta$ -Aminocrotonate and Analogous Compounds.** ERICH BENARY (*Ber.*, 1909, 42, 3912—3925).—The action of chloroacetyl chloride on  $\beta$ -ketonic acid esters proceeds only

with difficulty, and does not lead to uniform products, owing to the acid nature of the ester. The  $\beta$ -amino-ketonic acid esters enter more readily into the reaction. Ethyl  $\beta$ -aminocrotonate reacts with chloroacetyl chloride in molecular proportions to form a crystalline chloroacetyl product, which is obtained in quantity when the operation is performed in presence of pyridine. The chloroacetyl group is attached to carbon,  $\text{NH}_2 \cdot \text{CMe} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , since, on heating, ethyl chloride and a neutral compound,  $\text{C}_6\text{H}_5 \cdot \text{O}_3\text{N}$ , are formed, which later is converted by sodium hydroxide into  $\alpha$ -acetyl tetronic acid,



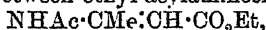
ammonia being eliminated. Ethyl  $\beta$ -anilinoacetonate similarly forms a *C*-chloroacetyl derivative, likewise acetylacetanamine,



Acetic anhydride in presence of pyridine acts on ethyl  $\beta$ -aminocrotonate to give an acetyl derivative isomeric with that obtained by Collie (Abstr., 1885, 373), to which he assigned the formula of an *N*-derivative,  $\text{COMe} \cdot \text{NH} \cdot \text{CMe} : \text{CH} \cdot \text{CO}_2\text{Et}$ . This new isomeride is formed in presence of an excess of the base, but is easily converted into the older form. The isomerism is chemical and not physical. In a similar manner two isomeric benzoyl derivatives are formed, that prepared in presence of pyridine easily passing over into the other. Both isomerides yield benzamide when hydrolysed with acids, and accordingly both are *N*-benzoyl derivatives. The isomeric acetyl compounds must also both be regarded as *N*-derivatives, but no *N*-chloroacetyl compound could be obtained.

Ethyl  $\beta$ -methylaminocrotonate yielded only one acetyl and one benzoyl derivative. Both these are *C*-derivatives; the latter forms benzoylacetone and acetophenone when hydrolysed, gives ethyl diphenylmethylpyrazolecarboxylate with phenylhydrazine and ethyl 3-phenyl-5-methylisooxazole-4-carboxylate,  $\text{N} < \begin{array}{c} \text{O} - \text{CMe} \\ \text{CPh} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array}$  with hydroxylamine. The acetyl derivative under like conditions gives rise to ethyl 1-phenyl-3:5-dimethylpyrazole-4-carboxylate and ethyl 3:5-dimethylisooxazole-4-carboxylate.

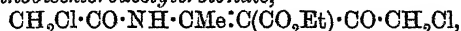
The isomerism of the two *N*-acetyl derivatives may be due either to structural isomerism between ethyl acylaminocrotonate,



and ethyl acyliminobutyrate,  $\text{NAc} : \text{CMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , or to *cis*- and *trans*-configuration of the ethylene carbon atom in the first of these formulæ.

Ethyl  $\beta$ -amino- $\alpha$ -chloroacetylcrotonate crystallises in colourless, long needles, m. p. 127—128°, when quickly heated. The fused mass solidifies to  $\alpha$ -acetyltetronamide.

Ethyl  $\beta$ -aminobischloroacetylcrotonate,

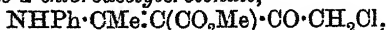


crystallises in colourless needles, m. p. 78°. It is readily decomposed by alkalis, yielding the monoacetyl compound.

$\alpha$ -Acetyltetronamide,  $\text{NH}_2 \cdot \text{CMe} : \text{C} < \begin{array}{c} \text{CO} \cdot \text{O} \\ \text{CO} \cdot \text{CH}_2 \end{array}$ , crystallises in needles,

which become brown at  $200^{\circ}$ , m. p.  $230-231^{\circ}$  (decomp.). *a*-Acetyl-tetronic acid, prepared by hydrolysis of the amide, separates in colourless needles, m. p.  $79.5-80.5^{\circ}$ ; the light blue copper salt has decomp.  $275-280^{\circ}$ . The anilide forms soft, colourless needles, m. p.  $188-189^{\circ}$ .

*Methyl  $\beta$ -anilino- $\alpha$ -chloroacetylcrotonate*,

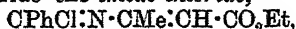


crystallises in radially-grouped needles, m. p.  $59-60^{\circ}$ .

*$\alpha$ -Chloroacetylacetylcetonamine*,  $\text{NH}_2 \cdot \text{CMe} \cdot \text{CAc} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , crystallises in thick rods, m. p.  $71^{\circ}$ .

*Ethyl  $\beta$ -amino- $\alpha$ -acetylcrotonate*, prepared by acetylation with pyridine and acetyl chloride, forms small, prismatic granules, m. p.  $109-110^{\circ}$ . When heated with acetic anhydride or dissolved in acetyl chloride, it is converted into the  $\beta$ -isomeride, m. p.  $63^{\circ}$  (Collie, *loc. cit.*).

*Ethyl  $\beta$ -amino- $\beta$ -benzoylcrotonate*, prepared by the action of benzoyl chloride and pyridine on the base, crystallises in four-sided plates, m. p.  $95-96^{\circ}$ . It passes into the  $\beta$ -isomeride when heated above  $200^{\circ}$  or when dissolved in acetyl chloride. When warmed with phosphorus pentachloride the imide chloride,



is obtained, crystallising in colourless needles, m. p.  $98-99^{\circ}$ .

*Ethyl  $\beta$ -amino- $\beta$ -benzoylcrotonate* forms short, hard, irregular crystals, m. p.  $46-48^{\circ}$ ; it is obtained also by the condensation of benzamide with ethyl acetoacetate in presence of aluminium chloride. It yields the same imide chloride as the  $\alpha$ -isomeride. Both isomerides yield benzamide when boiled with sulphuric acid.

*Ethyl  $\beta$ -methylamino- $\alpha$ -acetylcrotonate*,  $\text{NHMe} \cdot \text{CMe} \cdot \text{CAc} \cdot \text{CO}_2\text{Me}$ , forms four-sided prisms, m. p.  $54-55^{\circ}$ .

*Ethyl  $\beta$ -methylamino- $\alpha$ -benzoylcrotonate* forms platelets, m. p.  $69-70^{\circ}$ , and reacts with hydroxylamine, forming *ethyl 3-phenyl-5-methylisoxazole-4-carboxylate*, which crystallises in needles, m. p.  $49-50^{\circ}$ ; the corresponding acid has m. p.  $188-189^{\circ}$ , and decomp.  $260^{\circ}$ .

E. F. A.

**Electrolytic Reduction of Aldehyde Ammonias in Sulphuric Acid Solution.** PETER KNUDSEN (*Ber.*, 1909, 42, 3994-4003. Compare D.R.-P. 175071; Loeb, *Abstr.*, 1899, i, 122; Brand, this vol., i, 784).—The electrolytic reduction of aldehyde ammonias takes place in presence of sulphuric acid and under such conditions that the compound is largely decomposed. When hexamethylenetetramine is electrolysed, using a lead cathode, the product is a mixture of mono-, di-, and tri-methylamine. A yield of some 50% of the mixed amines can be obtained, but the relative proportions depend on the conditions of the experiment. With small current densities (that is, twenty-four hours for 0.25 mol.) about equal quantities of the three amines are obtained, but with larger densities the proportion of methylamine is increased. The addition of formaldehyde to the electrolyte and the use of high current densities favour the formation of dimethylamine, whereas low current densities in the presence of formaldehyde favour the production of the tertiary amine. When ammonium sulphate is present, the yield of bases is decreased, more especially the yields of

secondary and tertiary amines. The electrolytic reduction of a mixture of ammonium sulphate and formaldehyde leads to the formation of amines; the yield, however, is only small. A mixture of methylamine and formaldehyde yields di- and tri-methylamine. In all the above experiments methyl alcohol is formed, and the yield varies with the conditions.

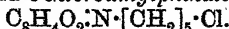
Aldehyde ammonia gives rise to ethylamine and diethylamine, but not to the formation of tertiary base. Hydrobenzamide yields benzylamine, and benzylidenemethylamine, benzylmethylamine.

The hydrolysing action of sulphuric acid on hexamethylenetetramine has been studied: at 18° the hydrolysis is nearly complete after one hour, but at 12° some three hours are required, and even then the reaction is not complete.

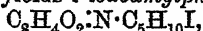
J. J. S.

**ζ-Amino-ketones.** SIEGMUND GABRIEL (*Ber.*, 1909, 42, 4050—4058. Compare Abstr., 1908, 181, 274, 464, 648, 649; this vol., i, 491, 492, 493).—It has not been found possible to synthesise methyl ζ-amino-hexyl ketone from ethyl acetoacetate and ε-iodobenzoylamylamine (von Braun and Steindorff, Abstr., 1905, i, 206), but it can be prepared from ethyl malonate and ζ-phthaliminoheptoyl chloride or from ethyl acetoacetate and ε-iodoamylphthalimide.

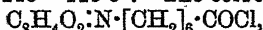
α-Dichloropentane and potassium phthalimide react at 180°, yielding a small amount of pentamethylenediphtalimide (von Braun, Abstr., 1904, i, 1019) and ε-chloroamylphthalimide,



The latter has m. p. 30—31°, and when boiled with an alcoholic solution of sodium iodide yields ε-iodoamylphthalimide,



which crystallises in compact, pointed prisms, m. p. 75—76°. The iodo-compound reacts with ethyl malonate and sodium ethoxide, yielding ethyl ε-phthalimino-amylmalonate, which gives the corresponding acid,  $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_5\cdot\text{CH}(\text{CO}_2\text{H})_2$ , when hydrolysed with hydriodic acid. The acid crystallises in rectangular plates, m. p. 153° (decomp.), and when heated at 170° yields ζ-phthaliminoheptonic acid,  $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$ , which crystallises in flat, pointed needles, m. p. 115—115.5°. The corresponding chloride,



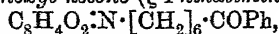
forms a crystalline mass of low m. p., and reacts with ethyl sodio-malonate in the presence of benzene, yielding a product from which methyl ζ-phthaliminoheptyl ketone,  $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot[\text{CH}_2]_6\cdot\text{COMe}$ , can be isolated after hydrolysis with hydriodic acid. The ketone crystallises in colourless plates or needles, m. p. 51°.

A better yield of the ketone is obtained by hydrolysing with hydriodic acid, ethyl phthaliminoamylacetoacetate, obtained by condensing ε-iodoamylphthalimide with potassium ethoxide and ethyl acetoacetate.

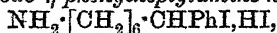
Methyl ζ-aminoheptyl ketone,  $\text{NH}_2\cdot[\text{CH}_2]_6\cdot\text{COMe}$ , is formed when the crude ethyl phthalimino-amylacetoacetate is hydrolysed with sulphuric acid. It is an oil with a strong amine odour. The *platinichloride*,  $2\text{C}_8\text{H}_{17}\text{ON}, \text{H}_2\text{PtCl}_6$ , is crystalline, and has m. p. 167—171° (decomp.). The *aurichloride* is not so soluble as the platini-

chloride and forms golden-yellow needles, m. p. 80°. The base combines with phenylthiocarbimide, yielding *phenyl-ζ-acetoheptylthiocarbimide*,  $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot [\text{CH}_2]_6 \cdot \text{COMe}$ , m. p. 77°.

*Phenyl-ζ-phthaliminohexyl ketone* (*ζ-Phthaliminohexophenone*),



obtained from phthaliminohexoyl chloride, benzene, and aluminium chloride, crystallises in glistening, flat needles, m. p. 96—97°, and, when hydrolysed with sodium hydroxide solution and then with 20% hydrochloric acid, yields *phenyl ζ-aminoheptyl ketone* as an oil which rapidly absorbs carbon dioxide. The *hydrochloride*,  $\text{C}_{13}\text{H}_{19}\text{ON} \cdot \text{HCl}$ , crystallises in oblong plates, m. p. 120°; the *aurichloride* has m. p. 106°, and the *platinichloride*, m. p. 213° (decomp.). When reduced with sodium and alcohol, the amino-ketone yields *η-hydroxy-η-phenylheptylamine*,  $\text{NH}_2 \cdot [\text{CH}_2]_6 \cdot \text{CHPh} \cdot \text{OH}$ , the *platinichloride* of which has m. p. 206° (decomp.). Concentrated hydriodic acid transforms the base into *η-iodo-η-phenylheptylamine hydriodide*,



in the form of needles, m. p. 109°. The corresponding *picrate*,  $\text{C}_{13}\text{H}_{20}\text{NI} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3 \cdot 2\text{H}_2\text{O}$ , crystallises in yellow needles, m. p. 84—85°.

The ζ-aminoheptophenone thus behaves quite differently from ε-aminoheptophenone when reduced.

J. J. S.

**Acid Properties of Halogenated Amides. Hofmann's Migration.** CHARLES MAUGUIN (*Compt. rend.*, 1909, 149, 790—793).

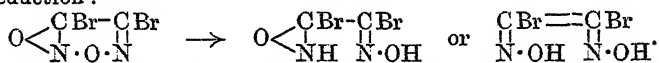
—On adding the calculated amount of bromoacetamide to a solution of sodium in absolute alcohol at  $-15^\circ$ , the *sodium* derivative,  $\text{COMe} \cdot \text{NNaBr}$ , is formed, and may be precipitated as a white powder by the addition of cooled, anhydrous ether. The sodium, *potassium*, and *barium* salts may also be prepared in aqueous solution, but are contaminated with alkali bromide. With silver nitrate the aqueous solutions give an insoluble, white *silver* derivative, which is violently explosive when dry.

The *sodium* derivatives of bromopropionamide and bromoisobutyramide have also been prepared at low temperatures. On attaining the ordinary temperature they undergo explosive decomposition, the metallic bromide with an alkyl cyanate being produced (compare Hofmann, *Abstr.*, 1882, 951). When allowed to decompose in presence of alcohol, substituted urethanes are formed. W. O. W.

**Fulminic Acid. IV. Action of Halogens on Mercury Fulminate.** HEINRICH WIELAND (*Ber.*, 1909, 42, 4192—4199. Compare this vol., i, 215, 369).—In the light of recent work on the so-called glyoxime peroxides (compare Wieland, Semper, and Gmelin, this vol., i, 609), the “dibromonitroacetonitrile” obtained by Kekulé (*Annalen*, 1858, 105, 279) by the action of bromine on mercury fulminate must be identical with dibromofuroxan,  $\text{O} < \begin{array}{c} \text{CBr} \cdot \text{CBr} \\ \text{N} \cdot \text{O} \cdot \text{N} \end{array}$ .

The fact that the interaction of dibromofuroxan and aniline yields oxanilidedioxime, instead of dianilinofuroxan (compare Holleman, *Abstr.*, 1893, i, 494), is explained by the formation of aniline-black in large proportions as a secondary product. By bromine-substitution of

the furoxan ring, the latter has assumed considerable oxidising power, so that, in the first phases of most of its reactions, the ring is opened by reduction :



When it is treated with nitrogen-bases, substitution then occurs, the products being amidoximes of oxalic acid. In consequence of the oxidising action, part of the base is oxidised in the case of aniline to aniline-black, and in those of hydrazine and ammonia to nitrogen. Only in the reaction with diethylamine does dibromofuroxan yield a compound in which the furoxan ring is unbroken.

Thus, with ammonia, dibromofuroxan yields nitrogen and oxamide-dioxime.

*Tetra-ethylloxamidedioxime*,  $\text{OH} \cdot \text{N} \cdot \text{C}(\text{NEt}_2) \cdot \text{C}(\text{NEt}_2) \cdot \text{N} \cdot \text{OH}$ , prepared by the action of diethylamine on dibromofuroxan, forms large, colourless plates, m. p.  $71^\circ$ .

*Tetra-ethyldiaminofuroxan*,  $\text{O} \begin{array}{c} \diagup \text{C}(\text{NEt}_2) \diagdown \\ \text{N} - \text{O} - \text{N} \end{array} \cdot \text{C}(\text{NEt}_2)$ , also obtained by

the interaction of diethylamine and dibromofuroxan, is a non-basic oil, with an odour resembling those of camphor and pyridine; it could not be obtained pure, as it decomposes at  $115^\circ$ .

In the interaction of chlorine and mercury fulminate, the oxidising action of the halogen results in the liberation of hydrogen chloride, and the principal result is the formation of a polymeride of fulminic acid. A small quantity of *dichlorofuroxan*,  $\text{O} \begin{array}{c} \diagup \text{CCl} \diagdown \\ \text{N} \cdot \text{O} \cdot \text{N} \end{array} \cdot \text{CCl}$ , was separated in an impure state from the products, which also contain cyanogen chloride, but trichloronitromethane is obtained in appreciable quantity only when excess of chloroform is allowed to act, without cooling, on the fulminate (compare Holleman, Abstr., 1892, 25).

In the action of bromine on mercury (or silver) fulminate, the first product is probably an additive product,  $(\text{CBr}_2 \cdot \text{N} \cdot \text{O})_2\text{Hg}$ , which loses mercuric bromide, giving the unstable bromoformnitrile oxide,  $\text{O} \begin{array}{c} \diagup \text{CBr} \diagdown \\ \text{N} \end{array}$ , 2 mols. of this compound then polymerising to dibromofuroxan.

A similar explanation holds for the action of chlorine on mercury fulminate, except that, in this case, the marked oxidising action of the halogen causes the predominance of the complete destruction of the fulminate molecule with formation of carbon dioxide. T. H. P.

**Formation of "Nitrolime" (Calcium Cyanamide). II.** FRITZ FOERSTER and HANS JACOBY. (*Zeitsch. Elektrochem.*, 1909, 15, 820. Compare Abstr., 1907, i, 397).—It is found, in agreement with earlier experiments, that when mixtures of calcium carbide and calcium fluoride are heated in an atmosphere of nitrogen for two hours at  $800^\circ$  to  $900^\circ$ , the greatest amount of nitrogen is taken up by the mixtures containing between 2% and 5% of the fluoride. If the time of reaction is increased to eight or ten hours, however, this difference disappears, all the mixtures taking up the same quantity of nitrogen. At  $840^\circ$

the limit is reached at about 11%, and at 860° at 15%, of nitrogen in the product (complete conversion would correspond with 25.5%). The rate of absorption of nitrogen is proportional to its pressure (for pressures near 1 atmosphere). The rise of temperature which occurs when a considerable quantity of calcium carbide reacts with nitrogen is measured by heating 200 grams of carbide in a well-closed graphite crucible to the temperature at which reaction just begins, and then removing the blowpipes used for heating. With ordinary calcium carbide alone, the reaction begins at 1000°, and the temperature then rises to 1180°. With a mixture containing 5% of calcium chloride the reaction begins at 640°, and the temperature rises to 1010°. With 5% of calcium fluoride the reaction begins at 840°, and the temperature rises to 980°. In no case does the initial rapid reaction complete the conversion of the carbide; further heating is always necessary. The reaction in the case of the calcium fluoride mixtures is, however, much more under control than in the other cases, and by careful regulation of the heat, the whole conversion may be completed without exceeding a temperature of 960°.

The details of a number of experiments with charges of 80 to 90 kilograms, which were made by F. Carlson, are given; these confirm the conclusions drawn from the smaller experiments.

The technical method of preparing calcium cyanamide by heating an electrical resistance in the axis of a cylindrical mass of calcium carbide exposed to nitrogen is described. An experiment shows that the reaction develops enough heat to propagate itself to a short distance from the heated portion.

Careful estimations of the cyanide present show that the addition of calcium chloride or calcium fluoride does not increase the quantity of it (0.017 to 0.025% of hydrogen cyanide is found). In presence of excess of an alkali chloride, however, very considerable quantities are produced.

T. E.

**Reaction between Hydrogen Sulphide and Cyanaminodithiocarbonates.** ARTHUR HANTZSCH (*Ber.*, 1909, 42, 4215—4216).—The salt obtained by the action of hydrogen sulphide and potassium cyanaminodithiocarbonate, which the author and Wolvekamp (*Abstr.*, 1904, i, 718) regarded as a salt of thiocarbamidodithiocarbonic acid,  $C(SH)_2 \cdot N \cdot CS \cdot NH_2$ , has now been shown by Rosenheim, Levy, and Grünbaum (this vol., i, 776) to be a salt of trithioallophanic acid. As thiocarbamidodithiocarbonic acid is isomeric with trithioallophanic acid,  $SH \cdot CS \cdot NH \cdot CS \cdot NH_2$ , these authors are, however, inaccurate in stating that the latter acid is a reduction product.

T. H. P.

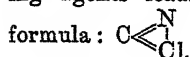
**History of Guanino-acids.** EMIL FISCHER (*Zeitsch. physiol. Chem.*, 1909, 63, 235—236. Compare Gansser, this vol., i, 702, and H. Ramsay, *ibid.*, i, 88).—The author objects to the name ethyl chloroformate for ethyl chlorocarbonate or the name ethyl guaninoformate for ethyl methylcarbamate. There is a considerable difference in properties between the carbamic esters and glycine esters. Glycine ester and not urethane is to be regarded as the first member of the series of esters of amino-acids.

J. J. S.

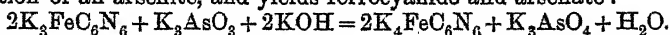
**Preparation of Cyanides.** NIKODEM CARO (D.R.-P. 212706).—The alkali and alkaline earth cyanides are prepared by heating the carbonate of the metal with carbon in the presence of an alkaline fluoride (instead of a chloride) at 900—1100°. The employment of a fluoride enables the reaction to proceed below the melting point of the mixture; a porous mass is formed which facilitates the absorption of nitrogen. Moreover, since the fluorides are sparingly soluble only, the required product is dissolved by water; the residue is dried, and employed in subsequent operations. F. M. G. M.

**Action of Alkaline Reducing Agents on Cyano-derivatives.** AUGUST GUTMANN (*Ber.*, 1909, 42, 3623—3631. Compare this vol., i, 144).—The behaviour of the cyanogen halides towards alkaline reducing agents (sodium arsenite, sulphide, sulphite, and plumbite) has been studied. All three halogen derivatives react with an alkaline solution of sodium arsenite, yielding sodium arsenate, cyanide, and halide. With cyanogen iodide, the reaction proceeds according to the equation:  $\text{CNI} + \text{Na}_3\text{AsO}_3 + \text{Na}_2\text{O} = \text{Na}_3\text{AsO}_4 + \text{NaCN} + \text{NaI}$ , and the method may be used for estimating cyanogen iodide. An aqueous solution of potassium sulphide reacts with cyanogen iodide according to the equation:  $\text{CNI} + \text{K}_2\text{S} = \text{KCN} + \text{KI}$ . When alcoholic solutions are used, a deep yellow coloration is formed together with a precipitate of potassium cyanide, but both coloration and precipitate disappear on the addition of water. It is suggested that the yellow coloration is due to the formation of potassium disulphide,  $\text{K}_2\text{S}_2$ , or of potassium sulphide,  $\text{K}_2\text{S}$ . Sodium plumbite reacts according to the equation:  $\text{CNI} + \text{Na}_2\text{PbO}_2 = \text{NaCN} + \text{PbO}_2 + \text{NaI}$ . Cyanogen chloride and sodium sulphite yield sodium sulphate, cyanide, and chloride. As the rule, the reactions with the bromide and chloride are analogous to those with the iodide.

The behaviour of the halogen compounds towards these reducing agents leads the author to suggest the following structural



Sodium arsenite and sulphite are not oxidised by cyanogen, but sodium sulphide and cyanogen yield cyanide and thiocyanate:  $\text{C}_2\text{N}_2 + \text{Na}_2\text{S} = \text{NaCN} + \text{NaCNS}$ . Potassium ferricyanide oxidises an alkaline solution of an arsenite, and yields ferrocyanide and arsenate:



Mercuric fulminate and sodium arsenite yield mercury, sodium arsenate, and cyanide.

It appears that compounds of the hydrogen peroxide type, for example, organic disulphides, sulphoxides, and disulphoxides, do not react with the above alkaline reducing agents, whereas compounds which are not of the hydrogen peroxide type, for example, sodium thiosulphate or its ester salts, readily yield an atom of oxygen or sulphur to these reducing agents. J. J. S.

**Action of Hydrobromic Acid on Allyl Cyanide.** BRULÉ (*Bull. Soc. chim.*, 1909, [iv], 5, 1019—1022).—Lespieau has shown (*Abstr.*, 1905, i, 9) that allyl cyanide when treated with hydrobromic

acid yields  $\beta$ -bromobutyramide. It was, therefore, of interest to ascertain whether Schindler's crotonitrile (Abstr., 1892, i, 32) would also yield  $\beta$ -bromobutyramide with hydrobromic acid, and this proves to be the case. Similarly, crotonic acid combines with hydrogen bromide to furnish  $\beta$ -bromobutyric acid, and not the  $\alpha$ -isomeride as stated by Hemilian (Abstr., 1874, 682).

Lespieau also found (Abstr., 1903, i, 684) that the principal product of the action of bromine on allyl cyanide is  $\beta\gamma$ -dibromobutyronitrile, with some monobromo-unsaturated compounds, whereas in the same reaction, Palmer (Abstr., 1889, 686) and Lippmann (Abstr., 1892, i, 27) had obtained  $\alpha\beta$ -dibromobutyronitrile as the principal product. The author now finds that all three products may be obtained by the action of bromine on allyl cyanide, and that the relative proportion of each formed depends on the age of the allyl cyanide used and the amount of bromine present, the  $\alpha\beta$ -isomeride being produced in largest quantity when old cyanide is used, or in presence of excess of bromine, or under experimental conditions leading to the formation of much hydrogen bromide. The mono-bromo-unsaturated products formed probably include a *product* of the formula  $\text{CHMe}:\text{CBr}:\text{CN}$  or  $\text{CH}_2:\text{CH}:\text{CHBr}:\text{CN}$ , since the portion boiling about  $50^\circ$  gives  $\alpha\beta$ -dibromobutyric derivatives with hydrobromic acid.

When  $\beta\gamma$ -dibromobutyramide is treated with zinc dust in alcohol, *vinylacetamide* is formed. This has m. p.  $72-73^\circ$ , and crystallises in colourless leaflets. Contrary to the experience of Beilstein and Wiegand (Ber., 1884, 17, 2008), the author finds that crotonamide can be prepared by distilling ammonium crotonate. T. A. H.

**Oxidation of Naphthene and Benzene Hydrocarbons by the Action of Air in Presence of Alkali.** K. W. CHARITSCHKOFF (*Chem. Zeit.*, 1909, 33, 1165).—Petroleum hydrocarbons (naphthenes) on oxidation by means of air with alkali as a "contact" substance, as used by Schall, give naphthenic acid, and, in addition, viscous, reddish-brown acids, which are soluble in ether or carbon disulphide, but insoluble in light petroleum. They reduce Fehling's solution and ammoniacal silver nitrate, but the presence of a  $\cdot\text{CHO}$  group could not be proved. The acids furnish viscous esters, and on exposure to air, especially in contact with alkalis, darken and resinify to asphalt-like products, whence it is proposed to call them "asphaltogenic" or polynaphthenic acids. They contain 4 atoms of oxygen per mol., two of which are in hydroxyl groups, and to these the pseudo-acid properties of the substances are due. A hydrocarbon,  $\text{C}_{10}\text{H}_{20}$ , b. p.  $169-171^\circ$ , isolated by careful fractionation of petroleum, gave on oxidation by this method at  $150^\circ$  a syrupy acid,  $\text{C}_{20}\text{H}_{20}\text{O}_4$ , and a similar *product* was obtained from synthetic menthane. From another decanaphthene, b. p.  $164-168^\circ$ , isolated from petroleum, an acid,  $\text{C}_{24}\text{H}_{24}\text{O}_4$ , was prepared.

Cymene gave cunic acid, whilst  $\psi$ -cumene gave three isomeric monobasic acids. Of the three xylenes, only the para-isomeride was attacked, yielding a monobasic acid. Benzenoid hydrocarbons therefore yield only simple monobasic acids by this method, whilst the naphthenes yield the complex acids described above. T. A. H.

**Systems formed by Aluminium Chloride and Bromide with Aromatic Hydrocarbons.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1089—1110).—The author discusses the investigations of Gustavson and others (*Abstr.*, 1903, i, 470, 804; 1908, i, 328) on the formation of compounds of aluminium chloride with hydrocarbons which act as ferments in synthetical reactions, and gives the results of his own investigations of the equilibria of systems composed of benzene or toluene and aluminium chloride or bromide.

A solution of aluminium chloride in benzene saturated at (1) 80° contains 0.72%  $\text{AlCl}_3$ , and at (2) 17° contains 0.12%  $\text{AlCl}_3$ . With toluene the saturated solution contains 0.92%  $\text{AlCl}_3$  at 73°, and 0.26%  $\text{AlCl}_3$  at 17°. At higher temperatures, in sealed tubes, the solubilities are increased, but the solutions turn brown and the hydrocarbon enters into Friedel and Crafts' reaction.

Investigation of the system benzene-aluminium chloride by the method already described (see this vol., i, 900) yields a freezing-point diagram consisting of two curves meeting at the eutectic point, 1.8°, which corresponds with the composition  $\text{AlBr}_3 \cdot 9 \cdot 1\text{C}_6\text{H}_6$ . The crystalline phases of the two curves consist of benzene and aluminium bromide respectively, the diagram indicating that no compound is formed between the two constituents.

With the system toluene-aluminium bromide, the freezing-point diagram is similar to that obtained in the previous case, and indicates that no molecular compound is formed by the two constituents. Here the eutectic point was not observed, owing to the very low temperature at which toluene melts.

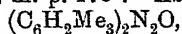
The system *p*-xylene-aluminium bromide gives similar results, the eutectic point, 10.2°, here corresponding with the composition  $\text{AlBr}_3 \cdot 7.47p\text{-C}_6\text{H}_4\text{Me}_2$ .

Investigation at different temperatures of the compounds  $\text{AlBr}_3 \cdot 3\text{C}_6\text{H}_6$  and  $\text{AlBr}_3 \cdot 3\text{C}_6\text{H}_5\text{Me}$ , formed in presence of hydrogen bromide (compare Gustavson, *Abstr.*, 1903, i, 470, 804), shows that the compositions of the two layers formed alter with change of temperature, indicating the formation of two immiscible solutions. It is possible, also, that the "ferments," if they exist as definite chemical compounds, dissolve with formation of two immiscible solutions. T. H. P.

**Constituents of Coal Tar. II—V.** GUSTAV SCHULTZ (*Ber.*, 1909, 42, 3602—3619. Compare this vol., i, 639).—II. *ψ-Cumene*. [With E. HERZFELD.]—The sulphonic acid obtained by Jacobsen's method (*Annalen*, 1877, 184, 199) is not pure, and it is necessary to recrystallise repeatedly before *ψ*-cumenesulphonic acid is obtained as well-developed, rhombic prisms resembling cubes. The hydrocarbon is obtained by heating the acid to 110°, and then passing over steam heated to 250°. In this manner, 150 grams of pure *ψ*-cumene were isolated from 1080 c.c. of crude oil, b. p. 165—170°. It has b. p. 166°/712 mm. and  $D^{25}_4$  0.877, and when oxidised with chromic anhydride yields trimellitic acid. When chlorinated in the dark, the hydrocarbon yields Haller's monochloro-derivative (*Abstr.*, 1885,

523), and ultimately *trichloro-ψ-cumene*,  $C_6Cl_3Me_3$ , which crystallises from alcohol in glistening needles, m. p. 197°.

When nitrated by a method similar to that used in the case of ethylbenzene, but keeping the temperature at 20° and stirring for some time, a good yield of the 5-nitro-derivative is obtained (*Zeitsch. Chem.*, 1867, 12), and, when this is oxidised, *nitrotrimellitic acid*,  $NO_2 \cdot C_6H_3(CO_2H)_3$ , is formed. The acid crystallises from hot water in long, glistening needles, m. p. 175°. *Azoxy-ψ-cumene*,



obtained by reducing the nitro-compound with sodium methoxide, crystallises from alcohol in pale yellow needles, m. p. 66°. When the nitro-ψ-cumene is further nitrated, 3:5-dinitro-ψ-cumene,  $C_9H_{10}O_4N_2$ , yellow needles, m. p. 171—172°, is formed, and ultimately 3:5:6-trinitro-ψ-cumene (Fittig and Laubinger, *Annalen*, 1869, 151, 261). It has not been found possible to nitrate ψ-cumene in the side-chains.

III. *n-Decane*. [With E. HARTOGH] (compare Jacobsen, *loc. cit.*; Krafft, *Abstr.*, 1882, 1271; 1883, 1076; Mabery, 1897, i, 450).—The fraction 150—180°, after repeated treatment with sulphuric acid and then with nitric acid, gave an oil (*n*-decane) with b. p. 172° when distilled over sodium, and  $D^{15}_D$  0.7387. The monochloro-derivative had b. p. 122°/50 mm. and  $D^{20}_D$  0.8868, and the dichloro-derivative, b. p. 157—159°/50 mm. and  $D^{19}_D$  1.0098. When boiled with barium hydroxide solution, the monochloro-derivative gave decyl alcohol, b. p. 120°/15 mm., m. p. 6.5°, and  $D^{17}_D$  0.8321. When oxidised with permanganate, the alcohol gave *n*-hexoic acid, m. p. 30°.

IV. *New Constituents of Solvent Naphtha*. [With A. PERL].—When solvent naphtha is fractionated, an oil is obtained intermediate between xylene and the trimethylbenzenes. From this oil the following fractions have been obtained: I, 153—157°; II, 157—160°; III, 160—162°. Fraction I was nitrated, reduced, and the resulting amino-compound benzoylated. From the crude benzoyl derivative, *p*-benzoylamino-*n*-propylbenzene, m. p. 115°, and benzoylamino-*p*-methyl-ethylbenzene, m. p. 165°, were isolated, together with two other benzoyl derivatives, m. p. 124° and 151°. Fractions II and III were fractionally sulphonated, the sulphonic acids transformed into the sulphonamides, and the non-sulphonated oils fractionated. Fraction II gave mesitylenesulphonamide and *o*-methylethylbenzenesulphonamide, together with an amide, m. p. 113—116°, and, as oils, *n*-decane and *p*-methylethylbenzene. Fraction III gave ψ-cumenesulphonamide, m. p. 181°, *m*-methylethylbenzenesulphonamide, m. p. 128°, *o*-methyl-ethylbenzenesulphonamide (oil), *p*-methylethylbenzenesulphonamide, m. p. 70°, and an amide, m. p. 169°, together with *n*-decane. *p*-Ethylbenzene is much more difficult to sulphonate than its isomerides.

V. *n-Propylbenzene*. [With J. FÜHRER].—Crude cumene contains appreciable amounts of *n*-propylbenzene, and Jacobsen's (*loc. cit.*) sulphonic acid contains *n*-propylbenzenesulphonic acid in addition to ψ-cumenesulphonic acid. To obtain the *n*-propylbenzene, the sulphonic acids are crystallised; after most of the ψ-cumenesulphonic acid has separated, the sulphuric acid is removed, and the acids converted into their barium salts. The readily soluble barium salt is transformed into the sodium salt, and then into the amide. This is crystallised

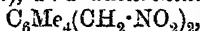
and the portion m. p. 112—116° heated with concentrated hydrochloric acid at 175°. The resulting oil is fractionated, and the portion with b. p. 159—161° is practically pure *n*-propylbenzene. The pure *sulphonamide* crystallises in plates, m. p. 112°. J. J. S.

**Durene.** RICHARD WILLSTATTER and HEINRICH KUBLI (*Ber.*, 1909, 42, 4151—4163).—All attempts to prepare a nuclear mononitrodurene have failed. Francis' method with benzoyl nitrate (*Trans.*, 1906, 89, 1) yields *ω*-nitrodurene,  $C_6H_2Me_3 \cdot CH_2 \cdot NO_2$ , m. p. 52.5°, b. p. 143—144°/10 mm., which separates from methyl alcohol in long, colourless prisms, has a not unpleasant sweet odour, and is slightly volatile with steam. Its solution in concentrated potassium hydroxide yields by dilution, cooling, and acidification by sulphuric acid an *isocompound*, m. p. 102—110°, which reverts readily into the more stable form. By nitration, the nitrodurene yields *ω*:3:6-*trinitrodurene*, m. p. 139°. *ω*-Aminodurene, m. p. 52°, obtained by reducing the nitro-compound by tin and hydrochloric acid, forms a *carbamate*,  $C_{21}H_{30}O_2N_2$ , m. p. 128—129°; *hydrochloride*,  $C_{10}H_{15}N \cdot HCl$ , m. p. 275—276°, and an *acetyl* derivative, m. p. 143.5° (corr.). 6-Bromo-3-nitrodurene, m. p. 178—179°, obtained by the action of 98% nitric acid on bromodurene in the presence of chloroform and concentrated sulphuric acid, crystallises in pale yellow prisms. 2- or (3-)-Bromo-*ω*-nitrodurene, obtained together with the preceding compound from bromodurene by Francis' method, has m. p. 89—90.5°, and is also produced by brominating *ω*-nitrodurene in chloroform containing a trace of iodine.

*Dinitroduryl bromide*,  $C_6Me_3(NO_2)_2 \cdot COBr$ , m. p. 121.5°, is obtained by the action of cold fuming nitric acid on bromodurene or 6-bromo-3-nitrodurene, and yields dinitrodurylic acid by treatment with alcoholic potassium hydroxide. In a similar way the *bromide* of dinitrodimethylbenzenedicarboxylic acid,  $C_6Me_2(NO_2)_2(COBr)_2$ , m. p. 122°, is obtained. 3-Nitrodurene is produced by the interaction of iododurene and silver nitrite, but in such small amount that it cannot be isolated; its presence is proved by its reduction to 3-aminodurene. 3-Aminodurene, b. p. 261—262° (corr.), m. p. 75°, is obtained by reducing 6-bromo-3-nitrodurene by zinc dust in glacial acetic acid and concentrated hydriodic acid; the *hydrochloride* decomposes at 260°, and the *nitrate* at 200—205°; the *acetyl* derivative has m. p. 207°. It is easily oxidised to duroquinone.

Nitration by Francis' method does not yield *ω*-nitrated compounds in the case of *m*-xylene or mesitylene; with pentamethylbenzene, a mixture of about equal parts of *nitropentamethylbenzene*, m. p. 154°, and *ω*-nitropentamethylbenzene, m. p. 63°, is obtained, which is separated by means of methyl alcohol.

Hexamethylbenzene yields, by Francis' method, the *ether* of pentamethylbenzyl alcohol,  $O(CH_2 \cdot C_6Me_5)_2$ , m. p. 168°, and with an excess of benzoyl nitrate (2 mols.), *ω*:*ω*-dinitrohexamethylbenzene,



m. p. 139°.

C. S.

Hexahydrophenylacetylene [*cyclo*Hexylacetylene] and Hexahydrophenylpropionic Acid. GEORGES DARZENS and ROST (*Compt. rend.*, 1909, 149, 681—682. Compare *Abstr.*, 1907, i, 617).—When

cyclo-hexyl methyl ketone is treated with phosphorus pentachloride, an unstable dichloro-derivative is formed, which immediately loses hydrogen chloride, yielding  $\alpha$ -chlorocyclohexylethylene,  $C_6H_{11} \cdot CCl:CH_2$ , b. p.  $70-74^\circ/24$  mm. When this is heated on an oil-bath with excess of dry potassium hydroxide, cyclohexylacetylene,  $C_6H_{11} \cdot C:CH$ , is obtained as a mobile liquid having a characteristic odour, b. p.  $130-132^\circ$ . This compound forms a sodium derivative, from which hexahydrophenylpropionic [cyclohexylpropionic] acid has been obtained by Nef's action. The new acid occurs as an oily liquid, b. p.  $138-140^\circ/6$  mm.; its methyl ester has b. p.  $96^\circ/5$  mm.; the ethyl ester has b. p.  $105^\circ/5$  mm.

W. O. W.

**Kinetics of Bromination.** LUDWIK BRUNER and S. CZARNECKI (*Bull. Acad. Sci. Cracow*, 1909, 322-333).—The first part of the paper is polemical against Holleman (this vol., i, 93). In the second part an account is given of measurements of the velocity of bromination of ethylbenzene in glacial acetic acid solution in the dark. Experiments in the absence of, and in the presence of, hydrogen bromide or lithium bromide showed that these substances have no effect on the distribution of the bromine between the nucleus and the side-chain.

Toluene was also brominated electrolytically; the toluene formed a layer above a concentrated solution of hydrogen bromide, which was electrolysed between a zinc cathode and an anode either of platinum or carbon. At temperatures between  $90^\circ$  and  $100^\circ$ , substitution takes place practically only in the nucleus when the electrolysis is carried out in the dark or in a very weak light. In a bright light, however, practically only benzyl bromide is formed, no matter whether the temperature be low or high. These results are used to explain discrepancies between the observations of Cohen (*Trans.*, 1905, 87, 1034) and Holleman (*loc. cit.*).

T. S. P.

**Compounds of Aluminium Bromide with Nitro-compounds of Aromatic Hydrocarbons and their Derivatives.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1053-1089).—The author has investigated the freezing-point diagrams of the systems formed by aluminium bromide with nitrobenzene, and with each of the three chloronitrobenzenes, bromonitrobenzenes, and nitro-toluenes.

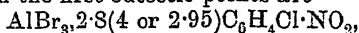
The diagram for the system  $AlBr_3 - C_6H_5 \cdot NO_2$  is typical for the case of two components forming one compound. The first eutectic point ( $C_6H_5 \cdot NO_2 - C_6H_5 \cdot NO_2, AlBr_3$ ) lies at  $-15^\circ$ , and corresponds with a composition represented by  $AlBr_3, 3C_6H_5 \cdot NO_2$ . The compound  $AlBr_3, C_6H_5 \cdot NO_2$ , representing the crystalline phase of the second portion of the curve, forms thin, pale yellow plates, m. p.  $87^\circ$ , and is decomposed by water with development of heat and liberation of nitrobenzene (compare Kohler, *Abstr.*, 1901, ii, 21). The second eutectic point ( $AlBr_3, C_6H_5 \cdot NO_2 - AlBr_3$ ) is about  $20^\circ$ , the composition corresponding with  $AlBr_3, 0.58C_6H_5 \cdot NO_2$ .

The three diagrams for the systems formed by aluminium bromide with the three chloronitrobenzenes are also typical for the formation of one definite compound between the two components. These crystalline compounds all have the formula  $AlBr_3, C_6H_4Cl \cdot NO_2$ ,

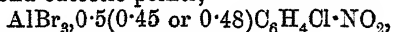
are extremely hygroscopic, and undergo instantaneous decomposition by the action of water. The m. p.'s of these compounds rise with the m. p. of the constituent chloronitrobenzene, as is seen from the following table :

	$\text{AlBr}_3, \text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$	$\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$
Ortho-.....	83.5°	32.5°
Meta-.....	103.5	44.5
Para-.....	115.0	83.0

The lack of complete proportionality between the m. p.'s of the chloronitrobenzenes and those of the compounds formed with aluminium bromide is conditioned probably by the varying stability of these compounds. This view is confirmed by comparison of the m. p.'s for the chloronitrobenzenes and their compounds with the eutectic temperatures, the greatest difference, namely, 95°, being observed between the m. p. of the compound and the second eutectic temperature for the system  $\text{AlBr}_3, p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ . The first eutectic temperatures are 13.8°, 35.5°, and 60°, and the second 21°, 40°, and 20°, for the ortho-, meta- and para-compounds respectively. The compositions corresponding with the first eutectic points are



and with the second eutectic points,



for the ortho-(meta- or para-)compound.

With aluminium bromide and the three bromonitrobenzenes, one molecular compound is formed in each case, its composition being  $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$ . The properties of these compounds are similar to those of the corresponding chloronitrobenzene compounds. The m. p.'s of the molecular compounds are 88.5° (38°), 122° (54°), and 144° (124.5°) respectively for the ortho-, meta-, and para-derivatives, the numbers in brackets representing the m. p.'s of the bromonitrobenzenes themselves. The differences between the m. p.'s of the compounds formed by aluminium bromide with bromonitrobenzene and with chloronitrobenzene are 5°, 18.5°, and 29° for the ortho-, meta-, and para-compounds, whilst the corresponding numbers for the bromo-, nitro-, and chloronitro-benzenes themselves are 5.5°, 9.5°, and 41.5°. The first eutectic temperatures for the systems  $\text{AlBr}_3\text{-}o\text{-(}m\text{ or }p\text{)-bromonitrobenzene}$  are 21°, 45.5°, and 98° respectively, these being lower than the m. p.'s of the bromonitrobenzenes by 17°, 8.5°, and 26.5° (the corresponding values for  $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$  being 18.7°, 9°, and 23°); the second eutectic temperatures are 24°, 42°, and 45°, which are lower by 63.5°, 80°, and 99° (the values for  $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$  being 62.5°, 63.5°, and 95°) than the m. p.'s of the corresponding compounds,  $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$ . The compositions at the first eutectic points are  $\text{AlBr}_3, 3.1(5.4 \text{ or } 2.4)\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$ , and at the second eutectic points,  $\text{AlBr}_3, 0.5(0.36 \text{ or } 0.42)\text{C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$ , for the *o*-(*m*- or *p*-)compound.

With *o*-, *m*-, and *p*-nitrotoluenes (m. p.'s -8.5°, +16°, and 53.5°), aluminium bromide forms the compounds  $\text{AlBr}_3, \text{C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ , m. p.'s 90°, 96°, and 88°; the low m. p. of the para-compound probably depends on its instability. The m. p.'s of the nitrotoluenes are higher by 2.5°, 15°, and 24.5° than the first eutectic temperatures (-11°, 1°, and 29°) of the systems  $\text{AlBr}_3\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$ , whilst the m. p.'s of the

compounds  $\text{AlBr}_3 \cdot \text{C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$  are higher than the second eutectic temperatures ( $19^\circ$ ,  $27^\circ$ , and  $27^\circ$ ) by  $71^\circ$ ,  $69^\circ$ , and  $61^\circ$  respectively. The compositions corresponding with the first and second eutectic temperatures are  $\text{AlBr}_3 \cdot 20 \cdot 4(4 \cdot 15 \text{ or } 2 \cdot 77) \text{C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$  and

$\text{AlBr}_3 \cdot 0 \cdot 51(0 \cdot 52 \text{ or } 0 \cdot 52) \text{C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$  for the ortho-(meta- or para-)compound. The composition at the first eutectic point for the system  $\text{AlBr}_3 \cdot o\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$  differs considerably from those for the meta- and para-systems, owing to the formation of the compound  $\text{AlBr}_3 \cdot 2o\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$  in addition to the normal compound,  $\text{AlBr}_3 \cdot o\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$ . The ready decomposition of the compound  $\text{AlBr}_3 \cdot p\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$  is indicated by the freezing-point diagram.

T. H. P.

**Benzyl Sulphoxide and  $\alpha$ -Hydroxybenzyl Sulphide.** EMIL FROMM and F. ERFURT (*Ber.*, 1909, 42, 3808—3812).—The constitution of benzyl sulphoxide has been established as  $\text{SO}(\text{C}_6\text{H}_5)_2$ , but Fromm and Ackert (*Abstr.*, 1903, i, 340) have observed the decomposition on heating to benzyl disulphide and benzaldehyde, and Smythe (*Trans.*, 1909, 95, 349) that the decomposition brought about by hydrogen chloride is very complicated. He explains this on the assumption that benzyl sulphoxide reacts in tautomeric forms, oxygen wandering from sulphur to carbon and forming  $\alpha$ -hydroxybenzyl sulphide,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{S} \cdot \text{C}_6\text{H}_5$ . Pummerer (*this vol.*, i, 580) criticises this view, but adopts another form of tautomerism.

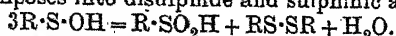
$\alpha$ -Hydroxybenzyl sulphide is obtained by the addition of benzyl mercaptan to benzaldehyde in long, colourless needles, m. p.  $43^\circ$ . It is entirely different from benzyl sulphoxide, and cannot be converted into this. It decomposes when warmed in benzene solution into benzaldehyde benzylmercaptal, and is decomposed by sodium hydroxide, towards which benzyl sulphoxide is stable.

Smythe's explanation is accordingly to be rejected, and the more probable tautomeric form of benzyl sulphoxide is  $\text{CHPh} \cdot \text{S}(\text{OH}) \cdot \text{CH}_2\text{Ph}$  (compare Pummerer, *loc. cit.*).

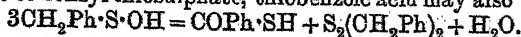
E. F. A.

**Hydrolysis of Thiosulphates and Thiosulphonates by Alkali.** EMIL FROMM and F. ERFURT (*Ber.*, 1909, 42, 3816—3822).—Price and Twiss (*Trans.*, 1908, 93, 1390) have isolated sodium sulphite, benzyl disulphide, and thiobenzoic acid as products of the hydrolysis of benzyl thiosulphate by sodium hydroxide. It is now shown that benzylsulphinic acid is also formed. Accordingly, both oxidation and reduction products of the thiosulphate are formed during hydrolysis. It may be assumed (compare Gutmann, *Abstr.*, 1908, i, 497) that an oxidising agent is formed during hydrolysis. This cannot well be benzyl disulphide, as Price and Twiss (*loc. cit.*) assume, as this compound does not react when boiled with benzyl chloride and sodium hydroxide. It is now assumed that the thiosulphate forms sulphite and thioalkyl peroxide:

$\text{NaO} \cdot \text{SO}_2 \cdot \text{SR} + \text{NaOH} = \text{Na}_2\text{SO}_3 + \text{R} \cdot \text{S} \cdot \text{OH}$ ,  
which last decomposes into disulphide and sulphinic acid:



In the case of benzyl thiosulphate, thiobenzoic acid may also be formed:



When sodium hydroxide is warmed with thiosulphonates, the solution is coloured yellow and contains sulphinic acids. Gutmann assumed the presence of sodium hydropersulphide,  $\text{NaOSH}$ , as an active agent in the reaction. This, however, in presence of excess of sodium hydroxide would become  $\text{Na}_2\text{SO}$ . By means of benzyl chloride it is possible to prove the presence of this substance if benzyl sulphoxide is formed. Actually by the hydrolysis of sodium *p*-tolylthiosulphonate by sodium hydroxide in presence of benzyl chloride, the following products are obtained: *p*-tolylsulphinic acid, benzyl disulphide, *p*-tolylbenzylsulphone, and *p*-tolylsulphonic acid.

E. F. A.

**Action of Formaldehyde and Alkali on Sulphones.** EMIL FROMM and F. ERFURT (*Ber.*, 1909, 42, 3823—3826).—Diformal-dibenzylsulphone, obtained by boiling dibenzylsulphone with formaldehyde and alkali (Fromm and Gaup, *Abstr.*, 1908, i, 970), is extremely stable. It withstands boiling with concentrated nitric acid and fusion with potassium hydroxide, and distils without decomposition; it is not attacked by bromine in chloroform, but by the action of bromine in sunlight a sparingly soluble product, m. p.  $264^\circ$ , is obtained. When boiled with bromine, a mixture of bromides is obtained, the most sparingly soluble of which is *dibromodiformaldibenzylsulphone*, m. p.  $280^\circ$ .

*p*-Tolylbenzylsulphone, when boiled with formaldehyde, yields *diformal-p-tolylbenzylsulphone*, m. p.  $128^\circ$ , which is equally stable. Phenylbenzylsulphone reacts less easily with formaldehyde, but likewise yields *diformalphenylbenzylsulphone*, m. p.  $76^\circ$ .

Benzylmethylsulphone, tolylmethylsulphone, or phenyltolylsulphone do not react with formaldehyde. Nitrated sulphones are decomposed by the alkali; di-*p*-nitrodiphenylsulphone, for instance, yielded stilbene, *p*-nitrophenol, and a compound,  $\text{C}_{38}\text{H}_{30}\text{O}_7\text{N}_4\text{S}_8$ , m. p.  $322^\circ$ .

Apparently, sulphones react with formaldehyde and alkali when they contain one benzyl and one aromatic residue. Two aromatic residues without the benzyl group, or a benzyl residue without a second aromatic residue, oppose the reaction.

E. F. A.

**Action of *p*-Toluenesulphonyl Chloride on Thiocarbamide.** EMIL FROMM and R. HEYDER (*Ber.*, 1909, 42, 3804—3807).—By the action of *p*-toluenesulphonyl chloride on thiocarbamide, Remsen and Turner (*Abstr.*, 1901, i, 270) obtained dithiocarbamide dichloride,  $\text{C}(\text{NH}_2)_2\text{Cl}\cdot\text{S}\cdot\text{S}\cdot\text{CCl}(\text{NH}_2)_2$ . Storch (*Abstr.*, 1891, 548) terms the same compound, which he obtained by the action of oxidising agents on thiocarbamide in acid solution, carbamido-iminodisulphide, and formulates it as  $\text{NH}\cdot\text{C}(\text{NH}_2)_2\cdot\text{S}\cdot\text{S}\cdot\text{C}(\text{NH}_2)_2\cdot\text{NH}$ , the dichloride being identical with Remsen and Turner's compound. Storch's formula is in agreement with the decomposition of the compound by water or alkalis into sulphur, thiocarbamide, and cyanamide.

*p*-Toluenesulphonyl chloride also acts as an oxidising agent towards arylthiocarbamides, but it acts similarly to hydrogen peroxide or bromine, liberating sulphur, and does not give disulphides. From phenylthiocarbamide and *p*-toluenesulphonyl chloride, sulphur and the *hydrochloride* of diphenyldi-iminotetrahydrodiazothiole are obtained. The

free base crystallises in colourless needles, m. p.  $198^{\circ}$ , and is identical with that described by Hector (Abstr., 1889, 872; 1890, 526; 1892, 292) with m. p.  $181^{\circ}$ . This figure is an error, as a mixture of the base prepared by both methods shows m. p.  $198^{\circ}$ . The acetate forms colourless needles, m. p.  $240^{\circ}$  (Hector, 233 $^{\circ}$ ); the base forms an additive product with carbon disulphide (Hector, *loc. cit.*) crystallising in yellow needles, m. p.  $162^{\circ}$ .

It is considered that the first action of toluenesulphonyl chloride is to form the disulphide; this decomposes into sulphur, phenylthiocarbamide, and phenylecyanamide, from which the diazothiole is ultimately built up.

E. F. A.

**Behaviour of Unsaturated Groups in Quaternary Ammonium Salts and Tertiary Sulphonamides.** EDGAR WEDEKIND [with F. OBERHEIDE] (*Ber.*, 1909, 42, 3939—3941).—The author gives a brief account of certain observations similar to that of Emde (this vol., i, 565), who found that the ethylene linking of cinnamyltrimethylammonium chloride is not able to take up hydrogen and become saturated.

That the ammonium complex possesses the property of rendering a double carbon-atom linking resistant to saturation by hydrogen has already been demonstrated, for example, by the preparation of 1-allyltetrahydroquinoline from the iodoallyl derivative of quinoline by reduction with tin and hydrochloric acid. It appears also that the double linking between carbon and oxygen is protected against reduction by the ammonium residue, since attempts to reduce, by means of sodium amalgam, certain phenacylammonium salts,  $\text{NR}_3\text{X}\cdot\text{CH}_2\cdot\text{COPh}$  (compare Abstr., 1908, i, 878), to the corresponding carbinol salts,  $\text{NR}_3\text{X}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$ , and so form an asymmetric carbon atom in addition to the asymmetric nitrogen atom, resulted in all cases in a total decomposition of the keto-ammonium salt with formation of free base; neutral reducing agents were found to be without action.

Also, with certain derivatives of tervalent nitrogen, a double carbon-atom linking exhibits unexpected behaviour. Attempts to prepare allyl*isobutylamine* from *p*-toluenesulphoallyl*isobutylamide*, by heating with chlorosulphonic acid at  $130$ — $140^{\circ}$  (compare Marckwald and von Droste-Huelshoff, Abstr., 1899, i, 289), show that the removal of the toluenesulphonyl residue does not take place, owing to an effect of the double linking. This reaction is, however, effected by Hinsberg's method (Abstr., 1892, 64) of heating with hydrochloric acid under pressure, toluenesulphonic acid being removed, and the hydrochloride of the amine obtained in theoretical yield.

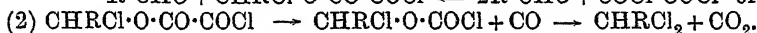
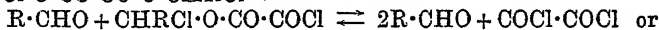
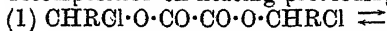
*p*-Toluenesulphoallyl*amide*,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{NS}$ , prepared by the action of dilute sodium hydroxide on *p*-toluenesulphonyl chloride and allylamine, forms colourless needles, m. p.  $64$ — $65^{\circ}$ .

*p*-Toluenesulphoallyl*isobutylamide*, prepared by the action of the calculated proportions of *isobutyl bromide* and alcoholic potassium hydroxide, is obtained as an oil; the hydrochloride has m. p.  $230^{\circ}$ .

*p*-Toluenesulphoisobutyl*amide*,  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{NS}$ , has m. p.  $78^{\circ}$ .

T. H. P.

**Oxalyl Chloride. III. Its Action on Carbonyl Compounds.** HERMANN STAUDINGER (*Ber.*, 1909, 42, 3966—3985. Compare *Abstr.*, 1908, i, 938; this vol., i, 796).—Oxalyl chloride behaves towards many carbonyl compounds like an inorganic acid chloride, such as phosphorus pentachloride, does, the carbonyl group being converted into  $\text{CCl}_2$ , thus:  $\text{CR}^1\text{R}^2\text{:O} + \text{COCl}\cdot\text{COCl} = \text{CR}^1\text{R}^2\text{Cl}_2 + \text{CO} + \text{CO}_2$ . The reaction has been studied for the following groups of ketonic derivatives: (1) Dibenzylideneacetone, dianisylideneacetone, benzylideneacetophenone, cinnamaldehyde, and benzylideneacetone; (2) benzaldehyde and benzophenone; (3) dimethylaminobenzaldehyde, dimethylaminobenzophenone, and tetramethyldiaminobenzophenone; (4) tetramethyldiaminodibenzylideneacetone and dimethylaminobenzylideneacetophenone. The ketochlorides of nearly all these compounds can be readily prepared by means of the above reaction, which proceeds in some cases in the cold and in others only on heating. An intermediate product is obtained only with cinnamaldehyde, its decomposition on heating proceeding in two ways:

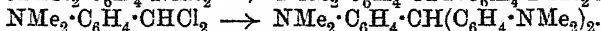
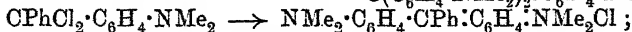
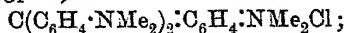


The ketochlorides corresponding with the compounds of group (1) are formed more readily than those of group (2), the cinnamenyl group increasing the reactivity of the carbonyl group towards oxalyl chloride. In other cases, also, a special influence of the cinnamenyl residue on neighbouring groups has been observed (compare Staudinger, *Abstr.*, 1908, i, 411; von Baeyer and Villiger, *Abstr.*, 1902, i, 380; von Baeyer, *Abstr.*, 1905, i, 281; Straus and Hüsey, this vol., i, 490). Also, the compounds of group (3) react far more readily than those of group (2), and the members of group (4) more readily than those of group (1), a dimethylamino-group in the para-position causing a marked increase in the reactivity of the carbonyl group.

The action of carbonyl chloride on the carbonyl group is similar to, but far less ready than, that of oxalyl chloride, the same products being obtained:  $\text{CR}^1\text{R}^2\text{:O} + \text{COCl}_2 = \text{CR}^1\text{R}^2\text{Cl}_2 + \text{CO}_2$ ; in no case is an intermediate product observed. Only the highly reactive compounds of groups (3) and (4) react readily with carbonyl chloride.

Of the various ketochlorides, only those with two dimethylamino-groups have a quinonoid character; the author ascribes to these compounds formulæ analogous to those suggested by von Baeyer for the triphenylmethane dyes (*Abstr.*, 1907, i, 757; compare also Schlenck, this vol., i, 808).

The ketochlorides of group (3) are regarded as intermediate products in the formation of triphenylmethane dyes, and, indeed, they react extremely readily with dimethylaniline according to the following schemes:  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CCl}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{Cl} \rightarrow$



The analogous conversion of the ketochlorides of group (4) into phenyldistyrylmethane and diphenylstyrylmethane dyes is to be investigated later.

The condensation *product* of oxalyl chloride and cinnamaldehyde:  $\text{CHPh}:\text{CH}:\text{CHCl}\cdot\text{O}\cdot\text{CO}\cdot\text{CO}\cdot\text{O}\cdot\text{CHCl}:\text{CH}:\text{CHPh}$ , forms white leaflets, m. p.  $106.5-107^\circ$  (decomp.), at which temperature it slowly, but almost quantitatively, loses  $\text{CO}$  and  $\text{CO}_2$ . It is extremely resistant to the action of water, but when heated with it, it yields oxalic acid; with aniline (6 mols.) in dichloroethylene, it gives oxanilide almost quantitatively, whilst with methyl alcohol it forms methyl oxalate and cinnamaldehyde.

Distyryldichloromethane, prepared from dibenzylideneacetone and oxalyl chloride in dichloroethylene solution, was obtained in pale yellow leaflets, m. p.  $72-74^\circ$  (von Baeyer and Villiger, Abstr., 1901, i, 658, gave  $78^\circ$ , and Straus and Ecker, Abstr., 1906, i, 859,  $77^\circ$ ).

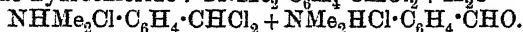
$\beta\beta$ -Dichloro- $\alpha\gamma$ -dianisylidenepropene,  $(\text{OMe}\cdot\text{C}_6\text{H}_4:\text{CH}:\text{CH})_2\text{CCl}_2$ , prepared from dianisylideneacetone and oxalyl chloride, forms white or faintly yellow crystals, m. p.  $86-87^\circ$ , and is stable when dry, but when moist, or in solution, immediately changes to a bluish-violet decomposition product, which is converted into the original compound by boiling with oxalyl chloride in ether or light petroleum.

Styryldichloromethane, prepared from cinnamaldehyde, has b. p.  $124^{12}/13$  mm., m. p.  $57.5-58.5^\circ$  (compare Charon and Dugoujon, Abstr., 1903, i, 240).

Phenylstyryldichloromethane,  $\text{CHPh}:\text{CH}:\text{CPhCl}_2$ , prepared from benzylideneacetophenone, has b. p.  $190-192^{16}/16$  mm., m. p.  $37.5-38^\circ$ .

Benzylideneacetone (2 mols.) and oxalyl chloride (1 mol.) react slowly in the cold, forming brownish-red needles, m. p.  $145-146^\circ$  (decomp.), the composition of which does not correspond with any simple product.

Dimethylaminobenzylidene chloride,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4:\text{CHCl}_2$ , obtained by the action of oxalyl chloride or carbonyl chloride on dimethylaminobenzaldehyde, forms colourless or faintly yellow plates, decomp. at  $60-65^\circ$  with evolution of hydrogen chloride, or at  $100-110^\circ$  in a sealed tube. It is extremely sensitive to the action of moisture, which changes it first to green and then to a yellow mixture of dimethylaminobenzylidene chloride hydrochloride and dimethylaminobenzaldehyde hydrochloride:  $2\text{NMe}_2\cdot\text{C}_6\text{H}_4:\text{CHCl}_2 + \text{H}_2\text{O} =$

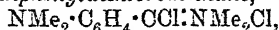


The action of moisture on the ethereal or light petroleum solution of dimethylaminobenzylidene chloride yields a dark green product, m. p.  $100-110^\circ$  (decomp.), which in some cases is composed of 1 mol. of dimethylaminobenzylidene chloride and 1 mol. of its hydrochloride, and is probably a quinhydrone-like compound formed by the union of the chloride in its quinonoid form,  $\text{NMe}_2\text{Cl}\cdot\text{C}_6\text{H}_4:\text{CHCl}$ , with its hydrochloride. With aniline (3 mols.), dimethylaminobenzylidene chloride yields dimethylaminobenzylideneaniline (compare Sachs and Lewin, Abstr., 1903, i, 37), whilst with dimethylaniline it gives a deep blue compound, which, with water, yields the white leucobase of crystal-violet, m. p.  $173^\circ$ . Dimethylaminobenzylidene chloride hydrochloride (*vide supra*), m. p.  $150-155^\circ$  (decomp.), is distinctly more stable than the free base. Dimethylaminobenzaldehyde hydrochloride (*vide supra*) forms white crystals, m. p.  $107-109^\circ$ , forms a

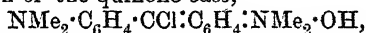
colourless solution in water, which decomposes it into the aldehyde, and does not react with dimethylaniline.

*Di- $\alpha$ -chlorophenyl dimethylaminophenylmethane*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPhCl}_2$ , prepared from dimethylaminobenzophenone, is readily acted on by moisture, and is obtained only in solution. Its *hydrochloride*,  $\text{C}_{15}\text{H}_{16}\text{NCl}_3$ , m. p.  $110-120^\circ$  (decomp.), is white and dissolves in water to a deep orange-red solution. *Dimethylaminobenzophenone hydrochloride*,  $\text{C}_{15}\text{H}_{16}\text{ONCl}$ , forms white crystals, m. p.  $129-130^\circ$ .

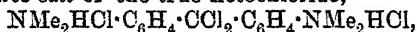
*Tetramethyldiaminodiphenyldichloromethane*,



prepared from tetramethyldiaminobenzophenone, best by the action of carbonyl chloride, separates in bluish-black, hygroscopic leaflets with green reflection, sinters at  $125-140^\circ$ , and decomp. at  $150^\circ$ . In water or alcohol it gives a deep blue solution, the colour disappearing gradually in the cold and rapidly on heating, the original ketone being formed. Addition of sodium hydroxide to its dilute solution results in the precipitation of the quinone *base*,



in violet-red flocks, m. p. (impure)  $150-160^\circ$  (decomp.). With dimethylaniline the ketochloride reacts instantaneously, giving crystal-violet. With aqueous hydrochloric acid, it forms a green *acid salt*,  $\text{NMe}_2\text{HCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CCl} : \text{C}_6\text{H}_4 : \text{NMe}_2\text{Cl}$ , whilst with dry hydrogen chloride it yields the white *salt* of the true ketochloride,



which turns dark blue at  $150^\circ$ , decomposes at  $185^\circ$ , and gives a deep blue aqueous solution.

On passing hydrogen chloride into a benzene or dichloroethylene solution of tetramethyldiaminobenzophenone, the solution at first turns brown, owing to the formation of the quinonoid mono-hydrochloride,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{OH}) : \text{C}_6\text{H}_4 : \text{NMe}_2\text{Cl}$ , and almost immediately afterwards colourless, consequent on the formation of the dihydrochloride, which decomposes at  $150^\circ$  in a vacuum, giving the ketone and hydrogen chloride; the dihydrochloride exhibits no inclination towards the quinonoid structure.

Tetramethyldiaminodistyryldichloromethane, prepared by the action of oxalyl chloride or carbonyl chloride on tetramethyldiaminodibenzylideneacetone, separates in the quinonoid form as a violet precipitate, dilute solutions of which are dark green and are changed to red by dilute hydrochloric acid.

Phenyldimethylaminostyryldichloromethane, prepared from dimethylaminobenzylideneacetophenone, has as yet only been obtained in solution.

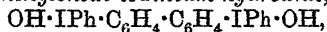
T. H. P.

**Homologue of Diphenyleneiodonium Hydroxide: Ditolyleneiodonium Hydroxide.** LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 190-194).—Diazotisation of 2 : 2'-diamino-4 : 4'-dimethyldiphenyl (compare von Niementowski, *Abstr.*, 1902, i, 21), followed by treatment with potassium iodide, yields: (1) a small proportion of 2 : 2'-di-iodo-4 : 4'-dimethyldiphenyl, which could not be purified, and (2) *ditolyleneiodonium iodide*,  $\begin{matrix} \text{C}_6\text{H}_3\text{Me} \\ | \\ \text{C}_6\text{H}_3\text{Me} \end{matrix} > \text{I} \cdot \text{I}$ , which forms

yellow crystals, m. p. 206° (decomp.) (compare Abstr., 1907, i, 1021; this vol., i, 94). T. H. P.

**Derivatives of 4:4'-Di-iododiphenyl with Polyvalent Iodine and the Iodination of Diphenyl.** CONRAD WILLGERODT and GUSTAV HILGENBERG (*Ber.*, 1909, 42, 3826—3833).—4:4'-Di-iododiphenyl (prepared by diazotising benzidine and decomposing the diazo-compound with potassium iodide) crystallises in colourless platelets, m. p. 202°. The *bisiododichloride*,  $\text{ICl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{ICl}_2$ , forms an amorphous, yellow precipitate (decomp. 154°); 4:4'-*di-iodosodiphenyl* was not obtained pure, the product exploded about 198°. 4:4'-*Di-iodoxydiphenyl*,  $\text{IO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}_2$ , obtained by boiling the iodochloride with sodium hypochlorite, is amorphous; it explodes at 218°, and, like the above compounds, gives only di-iododiphenyl when recrystallised.

*Diphenyl-4:4'-diphenylenedi-iodinium hydroxide*,



could only be obtained in aqueous solution of weak alkaline reaction. A number of salts are described: the *iodide* is a bright yellow, amorphous precipitate (decomp. 158°); the *bromide* is colourless, sinters at 170°, m. p. 185°; the *chloride* is also colourless, m. p. 185°; the *dichromate* is yellow and blackens at 80°; the *mercurichloride* is a colourless, amorphous compound, m. p. 170°; the *platinichloride* crystallises in golden-yellow needles, m. p. 168°.

The following salts of *di-p-tolyl-4:4'-diphenylenedi-iodinium hydroxide* have been prepared. The *iodide* is a light yellow, amorphous compound, m. p. 145°; the *bromide* is colourless, sinters at 180°, m. p. 186°; the *chloride* decomposes at 190°; the yellow *dichromate* sinters at 90°, m. p. 122°; the *mercurichloride* has m. p. 185°; the *platinichloride* is a yellowish-red precipitate, m. p. 173°.

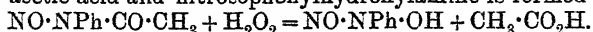
*Di-as-m-xylyl-4:4'-diphenylene-di-iodinium hydroxide* was obtained in solution with an alkaline reaction; the *iodide* forms a yellow, amorphous precipitate, m. p. 152°.

The dry iodinium compounds, when heated above their melting point, decompose into 4:4'-di-iododiphenyl and aryl iodides. This confirms their composition as diphenylene compounds, and not diphenyl-iodinium derivatives. Further, diphenyldi-iodochloride and mercury diphenyl give the same diphenyldiphenylenedi-iodinium chloride as obtained from di-iodosodiphenyl and iodobenzene.

When diphenyl is warmed in light petroleum solution with sulphur iodide and nitric acid, D 1.34, the product is di-iododiphenyl. When, however, nitric acid (D 1.5) is employed, the product is *p*-di-iodobenzene. This product also results when iodine and nitric acid (D 1.5) are used to introduce the halogen into diphenyl. E. F. A.

**Action of Hydrogen Peroxide on Nitrosoacetanilide and Spontaneous Decomposition of the Latter.** EUGEN BAMBERGER and OSCAR BAUDISCH (*Ber.*, 1909, 42, 3582—3591).—When hydrogen chloride is passed into a light petroleum solution of nitrosoacetanilide, acetanilide is formed, together with a small amount of a diazo-salt, but when the nitroso-derivative is oxidised with hydrogen peroxide at

-20° under suitable conditions, the acetyl group is eliminated in the form of acetic acid and nitrosophenylhydroxylamine is formed :



If the conditions which are described in detail are adhered to strictly, the yield of nitrosophenylhydroxylamine can be as high as 94% of the theoretical, but otherwise nitroso- and even nitro-benzene are formed by the oxidation of the nitrosohydroxylamine.

The hydroxylamine can be isolated in the form of its ammonium salt (compare this vol., i, 978) by passing a rapid stream of ammonia into a dry ethereal solution.

In a few of the experiments, hydrogen peroxide was practically without action on nitrosoacetanilide. *p*-Chloro- and *p*-bromo-nitrosoacetanilides are oxidised by hydrogen peroxide in much the same manner as nitrosoacetanilide.

*p*-Bromonitrosoacetanilide,  $\text{NO} \cdot \text{N}(\text{Ac}) \cdot \text{C}_6\text{H}_4\text{Br}$ , decomposes at 86—87°, and *p*-bromophenylnitrosohydroxylamine,  $\text{NO} \cdot \text{N}(\text{OH}) \cdot \text{C}_6\text{H}_4\text{Br}$ , has m. p. 86—87°.

Diphenyl is obtained when a benzene solution of nitrosoacetanilide is kept at the ordinary temperature (Abstr., 1898, i, 366), but when an ethereal solution is kept at 0°, a small amount of benzenediazonium nitrate is formed.

J. J. S.

**Amic Acids. V. Action of Amines on Dibasic Aliphatic Acids.** J. BISHOP TINGLE and S. J. BATES (*J. Amer. Chem. Soc.*, 1909, 31, 1233—1242).—In earlier papers (Tingle and Cram, Abstr., 1907, i, 692; Tingle and Lovelace, Abstr., 1907, i, 1044; Tingle and Rolker, this vol., i, 28; Tingle and Brenton, this vol., i, 798), experiments have been described on the interaction of amines with phthalic acid and its derivatives. The present paper gives an account of an extension of the work to aliphatic dibasic acids.

It has been found that the aliphatic amic acids,  $\text{NHR} \cdot \text{CO} \cdot \text{X} \cdot \text{CO}_2\text{H}$ , behave quite differently from the corresponding aromatic compounds. Under conditions in which the phthalamic acids are readily converted into imides, the aliphatic compounds are quite stable and cannot be transformed into the imides even by prolonged heating at a high temperature. The cause of this difference is discussed, and it is shown that it can only be due to the inherent nature of the benzene nucleus.

Oxanilic acid is not affected at 100° by ethyl alcohol, methyl alcohol, or toluene, but is converted by aniline into aniline oxanilate. *Quinoline oxanilate*, m. p. 122—123°, and the *pyridine* salt, m. p. 132—133°, form colourless crystals; the  $\beta$ -*naphthylamine* salt, m. p. 151°, forms pink crystals. *Potassium hydrogen oxanilate* was also prepared.

$\beta$ -Naphthylloxamic acid (Friedländer, Heilpern, and Spielfogel (Abstr., 1899, i, 708) could not be prepared.  $\beta$ -Naphthylsuccinamic acid melts at 184—185°, instead of 190—192°, as stated by Pellizzari and Matteucci (Abstr., 1888, 1303), and is not changed when heated at 100° with aniline, quinoline, or  $\beta$ -naphthylamine in presence of alcohol or toluene.

Fumaric acid combines with aniline at the ordinary temperature to

form *aniline hydrogen fumarate*, m. p. 185°, which forms colourless crystals. At 160–170°, aniline and fumaric acid yield anilino-succinylphenylimide (phenylasparaginil). Fumaranilic acid could not be obtained by Bischoff's method (Abstr., 1891, 1220), but was prepared by the action of fumaryl chloride on an ethereal solution of aniline. When either this compound or maleanilic acid is heated with aniline at 100°, phenylasparaginil is produced.

When a mixture of malic acid and aniline is distilled under reduced pressure, maleanilic acid and phenylasparaginil are produced. Maleanilic acid could not be prepared by Arppe's method (*Annalen*, 1856, 96, 111), but by warming the anil with strong potassium hydroxide solution and adding hydrochloric acid to the well-cooled product, small quantities of the acid were obtained, m. p. 155°; its *aniline salt* has m. p. 110°.

$\psi$ -Itaconanilic acid is not affected by aniline at 100°. Citraconic acid reacts with aniline to form a compound, m. p. 170–171°, which is probably anilinopyrotartaric acid. The statement of Gottlieb (*Annalen*, 1852, 77, 284), that when aniline and citraconic acid are heated together at 100° the anilic acid is produced, could not be confirmed.

Tartranilic acid yields salts with all the amines studied. The *aniline* and *quinoline* salts melt at 149–150° and 129–130° respectively. The  $\beta$ -naphthylamine salt, m. p. 176–177°, when heated at 180°, is converted into a compound, probably *phenyl- $\beta$ -naphthyltartramide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , m. p. 240–242°, which forms colourless crystals.  *$\beta$ -Naphthyltartramic acid*,

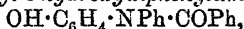
$\text{C}_{10}\text{H}_7 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CO}_2\text{H}$ , m. p. 180°, is obtained in small yield by heating  $\beta$ -naphthylamine with tartaric acid for three hours at 180–200°, and when heated at its m. p. is converted into the  *$\beta$ -naphthyltartramide*, m. p. 220°; the *aniline salt* melts at 172–174° with formation of *phenyl- $\beta$ -naphthyltartramide*.  
E. G.

[Preparation of Methylenebis-3-chloro-6-nitroaniline.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212594).—*Methylenebis-3-chloro-6-nitroaniline*,  $\text{CH}_2(\text{NH} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{NO}_2)_2$ , is prepared by heating 5-chloro-6-nitroaniline with formaldehyde at 70–80°. F. M. G. M.

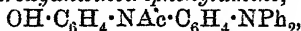
Electrochemical Reduction of Condensation Products of Aldehydes with Amines. WALTER LÖB (*Ber.*, 1909, 42, 3987).—Brand (this vol., i, 784) has overlooked the work of the author (Abstr., 1899, i, 122) and of Goecke (Abstr., 1903, i, 615) on this subject.  
T. H. P.

Diphenylamine and Acylperoxides. STEPHAN GAMBARJAN (*Ber.*, 1909, 42, 4003–4013).—Attempts have been made to prepare diphenylhydroxylamine by the oxidation of diphenylamine. Hydrogen peroxide is without action on the amine, and Caro's acid does not give definite products. With benzoyl peroxide in chloroform solution, the

chief product is *N*-benzoyl-*o*-hydroxydiphenylamine,

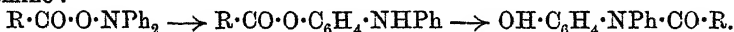


and with acetyl peroxide the products are *N*-acetyl-*o*-hydroxydiphenylamine, *N*-acetyl-*o*-hydroxyanilinotriphenylamine,

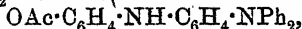


and tetraphenylhydrazine.

The acyl peroxide probably reacts with the amine, yielding free acid and acyldiphenylhydroxylamine,  $\text{R} \cdot \text{CO} \cdot \text{O} \cdot \text{O} \cdot \text{CO} \cdot \text{R} + \text{HNPh}_2 = \text{R} \cdot \text{CO} \cdot \text{OH} + \text{R} \cdot \text{CO} \cdot \text{O} \cdot \text{NPh}_2$ , the latter then undergoes molecular rearrangement, yielding an *o*-acyloxy-derivative of diphenylamine, and this, by a second rearrangement, yields an *o*-hydroxy-*N*-acyldiphenylamine:



The formation of the triphenylamine derivative can be accounted for by the following series of reactions. Two molecules of acetyldiphenylhydroxylamine undergo condensation, yielding acetic acid and  $\text{OAc} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NPh}_2$ . The latter is then transformed into



and this into  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NAc} \cdot \text{C}_6\text{H}_4 \cdot \text{NPh}_2$ . The tetraphenylhydrazine is probably formed by the condensation of acetyldiphenylhydroxylamine with the excess of diphenylamine:  $\text{NPh}_2 \cdot \text{OAc} + \text{HNPh}_2 = \text{AcOH} + \text{NPh}_2 \cdot \text{NPh}_2$ . *N*-Benzoyl-*o*-hydroxydiphenylamine dissolves in hot glacial acetic acid, and has m. p. 214°. When hydrolysed with methyl-alcoholic potassium hydroxide at 140° it yields *o*-hydroxydiphenylamine (Deninger, Abstr., 1894, i, 511), which, on acetylation, gives *N*-acetyl-*o*-hydroxydiphenylamine, m. p. 144–146°. The same acetyl compound is formed by the action of acetyl peroxide on diphenylamine, and crystallises from benzene. It dissolves in aqueous alkalis, but is precipitated by carbon dioxide.

*N*-Acetyl-*o*-hydroxyanilino-triphenylamine has m. p. 218–220°, and crystallises from glacial acetic acid.

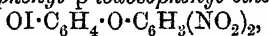
Diphenylamine and perbenzoic acid yield benzoic acid and an orange-red compound, m. p. 138–142°. J. J. S.

**Preparation and Hydrolysis of Phenylthiocarbimide Oxide.** EMIL FROMM and R. HEYDER (*Ber.*, 1909, 42, 3800–3803).—By the action of bromine on phenylthiocarbimide in chloroform solution in presence of aqueous ethyl alcohol, Freund and Bachrach (Abstr., 1895, i, 576, 578) obtained a bromine additive product of phenylthiocarbimide, and from this, phenylthiocarbimide oxide in small quantities. It is now found that the main product is a substance,  $\text{C}_9\text{H}_9\text{O}_2\text{NBr}_2$ , soluble in chloroform, crystallising in colourless needles. When methyl alcohol is used in the condensation, a corresponding compound,  $\text{C}_8\text{H}_7\text{O}_2\text{NBr}_2$ , m. p. 96°, is obtained, which is identical with methyl 2:4-dibromocarbanilate, described by Hentschel (Abstr., 1887, 143). The ethyl derivative is accordingly *ethyl* 2:4-dibromocarbanilate.

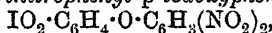
Phenylthiocarbimide oxide behaves on hydrolysis in agreement with the formula,  $\text{NPh} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{S} \end{smallmatrix}$ , assigned to it by Hantzsch and Wolve-

kamp (Abstr., 1904, i, 720). Potassium hydroxide in cold concentrated solution hydrolyses it to sulphur, diphenylcarbamide, and alkali sulphide. Phenylhydrazine gives rise to hydrogen sulphide and diphenylthiosemicarbazide. E. F. A.

**Derivatives of Aromatic *p*-Monoiodophenyl Ethers with Polyvalent Iodine.** CONRAD WILLGERODT and GUSTAV WIEGAND (*Ber.*, 1909, 42, 3763—3769).—as-m-Dinitrophenyl *p*-iodophenyl ether, prepared by adding potassium *p*-iodophenoxide to a cold alcoholic solution of chlorodinitrobenzene (1 mol.), forms pale yellow, lustrous needles of m. p. 156°. as-m-Dinitrophenyl *p*-iodochloride phenyl ether,  $\text{ICl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ , is obtained in the form of yellow needles by acting on a cold solution of the iodo-compound in chloroform with chlorine; it is very stable, and on heating it decomposes at 123°. as-m-Dinitrophenyl *p*-iodosphenyl ether,

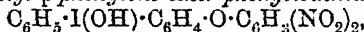


prepared by acting on the iodochloride with dilute sodium carbonate at the ordinary temperature, is a yellow, amorphous powder which decomposes at 131°. Attempts to prepare the iodoso-acetate were unsuccessful. as-m-Dinitrophenyl *p*-iodoxyphenyl ether,

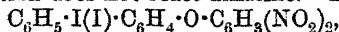


is obtained only in small quantities by boiling the iodoso-compound with water. A better result is obtained by digesting the iodochloride with sodium hypochlorite and acetic acid for one or two days at room temperature, and the yield is almost quantitative when the reaction mixture is boiled for ten to fifteen minutes instead. The pure iodoxy-compound is very stable; it crystallises in small, white needles, and explodes at 193°. This new method for preparing iodoxy-compounds was found to be equally satisfactory in the case of iodoxybenzene and *p*-iodoxytoluene.

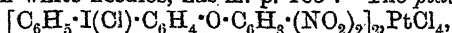
as-m-Dinitrophenyl *p*-phenylene-ether-phenyliodinium hydroxide,



is best prepared in solution by treating equimolecular quantities of dinitrophenyl *p*-iodoxyphenyl ether with silver oxide and water at 40—60°. The solution does not react alkaline. The iodide,



is prepared by rendering the solution of the base weakly alkaline with sodium carbonate, and then adding a concentrated solution of potassium iodide; it forms yellow needles of m. p. 159°. The chloride, similarly prepared, crystallises in white needles, and has m. p. 178°. The bromide, also in white needles, has m. p. 183°. The platinichloride,



obtained by mixing the aqueous solutions, has m. p. 180°. The mercurichloride of similar constitution has m. p. 185°. On mixing solutions of the iodium hydroxide and potassium dichromate, a pyrochromate,  $[\text{C}_6\text{H}_5 \cdot \text{I} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2]_2 \cdot \text{Cr}_2\text{O}_7$ , is precipitated; it has m. p. 112° (decomp.).

Picryl *p*-iodophenyl ether, prepared in a similar way to the dinitrophenyl ether, crystallises in large, yellow prisms, and has m. p. 136°. Picryl-*p*-iodochloridephenyl ether,  $\text{Cl}_2\text{I} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$ , was obtained in small, yellow needles, which decomposed at 151°. Iodoso-

and iodoxy-compounds of picryl *p*-iodophenyl ether could not be prepared.

*p*-Iodophenyl acetate,  $C_6H_4I \cdot OAc$ , was obtained from the interaction of potassium iodophenoxide and acetyl chloride in white, prismatic needles, which were so unstable that analysis was not possible. When the acetate was at once dissolved in chloroform and treated with chlorine, phenyl-*p*-iodochloride acetate was precipitated in small, yellow needles, which were as unstable as the iodo-compound itself, and were not analysed.

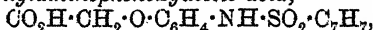
*p*-Iodophenyl benzoate, prepared from potassium iodophenoxide and benzoyl chloride, forms silvery, rhombic laminæ, and has m. p. 125°. Phenyl-*p*-iodochloride benzoate forms small, yellow needles, which decompose at 132°.

*p*-Iodosophenyl benzoate was not obtained in a pure state.

*p*-Iodoxyphenyl benzoate forms small, rhombic plates, which explode at 221°. Iodinium compounds could not be obtained. R. V. S.

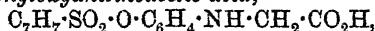
**Nitration of Certain Derivatives of *p*-Aminophenol.** FRÉDÉRIC REVERDIN [with A. DE LUC] (*Ber.*, 1909, 42, 4109—4184.\* Compare this vol., i, 377; *Abstr.*, 1907, i, 695).—Derivatives are now studied which contain the groups  $SO_2 \cdot C_7H_7$ ,  $CO \cdot C_6H_5$ , and  $CH_2 \cdot CO_2H$ , introduced two at a time alternately into the hydroxyl and amino-groups.

*p*-Toluenesulphonylaminophenoxyacetic acid,



prepared by heating *p*-toluenesulphonyl chloride, *p*-aminophenoxyacetic acid, and sodium acetate in alcoholic solution, forms colourless plates, m. p. 187°. The ethyl ester also forms colourless plates, m. p. 90°.

*p*-Toluenesulphonyloxylanilinoacetic acid,

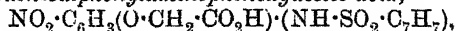


formed on heating *p*-hydroxyphenylglycine with *p*-toluenesulphonyl chloride and sodium hydroxide, crystallises in colourless needles, m. p. 161°. The ethyl ester has m. p. 205°; it is hydrolysed by alkali to ethyl *p*-hydroxyanilinoacetate, crystallising in colourless plates, m. p. 69°.

*p*-Benzoylamino-phenoxyacetic acid,  $CO_2H \cdot CH_2 \cdot O \cdot C_6H_4 \cdot NH \cdot CPh$ , prepared by the interaction of benzoyl chloride and *p*-aminophenoxyacetic acid, forms slightly violet-hued plates, m. p. 197°.

*p*-Benzoyloxyanilinoacetic acid,  $OBz \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H$ , forms colourless, prismatic, mother of pearl-like crystals, m. p. 165—171°.

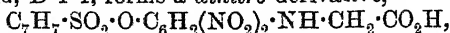
3-Nitro-4-toluenesulphonylaminophenoxyacetic acid,



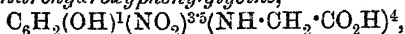
produced on nitrating with nitric acid, D 1.4, in acetic acid solution, forms almost colourless crystals, m. p. 158°, from alcohol. It crystallises from benzene in bright yellow, flat, prismatic needles. When hydrolysed by heating with concentrated sulphuric acid, 3-nitro-4-aminophenoxyacetic acid is obtained, crystallising in lustrous, brown needles, m. p. 185°. This is isomeric with the 2-nitro-compound obtained by Howard (*Abstr.*, 1898, i, 29). The barium salt forms bunches of lustrous, orange-coloured needles.

\* and *Arch. Sci. phys. nat.*, 1909, [iv], 28, 439—459.

*p*-Toluenesulphonyloxyanilinoacetic acid, when warmed at 60—70° with nitric acid, D 1·4, forms a *dinitro*-derivative,

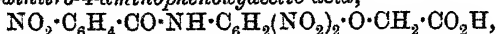


crystallising in almost colourless or light yellow, matted needles, m. p. 222° (decomp.). It is hydrolysed by sulphuric acid to a compound, assumed to be *dinitrohydroxyphenylglycine*,



which crystallises in blackish-brown needles with a metallic lustre, m. p. 176—177° (decomp.) and dissolves in dilute sodium hydroxide with a reddish-violet coloration. When nitric acid, D 1·52, is used for nitration, a *trinitro*-compound is formed, crystallising in matted needles, m. p. 194°. This yields the above-described *dinitro-p*-oxyphenylglycine on hydrolysis; accordingly, the third nitro-group is in the toluenesulphonyl nucleus, and the *trinitro*-derivative has the formula  $\text{NO}_2\cdot\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . The *dinitro*-derivative is obtained on nitration in acetic acid solution.

Nitric acid (D 1·4) acts on *p*-benzoylaminophenoxyacetic acid, forming a *mononitro*-derivative,  $\text{C}_6\text{H}_3(\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})(\text{NO}_2)(\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)^4$ , crystallising in minute, citron-yellow needles, m. p. 176—177°; on hydrolysis with sulphuric acid, it yields 3-nitro-4-aminophenoxyacetic acid. When nitration is effected in sulphuric acid solution by means of a mixture of nitric and sulphuric acids, a *trinitro*-derivative, *nitrobenzoyl-2:5-dinitro-4-aminophenoxyacetic acid*,



is formed, crystallising in citron-yellow needles, m. p. 206°, which yields 2:5-dinitro-4-aminophenoxyacetic acid, m. p. 170° (Reverdin and Bucky, Abstr., 1906, i, 748), on hydrolysis with sulphuric acid.

Nitration with acetic anhydride and nitric acid leads to a *trinitro*-compound, which was not obtained crystalline, probably containing the third nitro-group in the benzoyl radicle, since it yields 2:6-dinitro-4-aminophenoxyacetic acid,  $\text{C}_6\text{H}_2(\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})(\text{NO}_2)(\text{NH}_2)$ , crystallising in yellowish-brown plates, m. p. 176°, on hydrolysis.

*p*-Benzoyloxyanilinoacetic acid, when nitrated with nitric acid (D 1·4), forms a compound crystallising in citron-yellow needles, m. p. 189°, which, on hydrolysis, yields *dinitro-p*-hydroxyphenylglycine, m. p. 176—177°. A mixture of nitric and sulphuric acids yields products, m. p. 189° and 197°, which are a mixture of di- and tri-nitro acids. The chief product is *nitrobenzoyldinitrohydroxyanilinoacetic acid*. On hydrolysis, *dinitro-p*-hydroxyphenylglycine and nitrobenzoic acid are obtained.

The series of papers on the nitration of *p*-aminophenyl are briefly summarised. Nitration with nitric acid alone or in presence of acetic acid leads to mono- and *dinitro*-derivatives, which contain the nitro groups in positions 3 and 3:5. Acetyl and benzoyl derivatives give *dinitro*-compounds with the nitro-groups in 2:6. Compounds containing the radicles  $\text{Ph}\cdot\text{CO}$ ,  $\text{CH}_3\cdot\text{CO}$ ,  $\text{CH}_3$ , or  $\text{CH}_2\cdot\text{CO}_2\text{H}$ , yields mixtures of *dinitro*-derivatives with the nitro-groups in positions 3:5, 2:5, or 2:6.

E. F. A.

**Preparation of Arylalkyl-*p*-aminophenols.** CHEMISCHE FABRIK AUF ACTIEN (FORM. E. SCHERING) (D.R.-P. 211869).—When the con-

densation products from aromatic aldehydes and *p*-aminophenols are reduced with zinc in alkaline solution, they yield products which are employed for photographic purposes.

*Benzyl-p-aminophenol*, m. p.  $89^{\circ}$ , is obtained when benzylidene-*p*-aminophenol (30 parts) is reduced with zinc dust (15 parts) in alkaline solution, and the mixture afterwards acidified and extracted with ether. The *hydrochloride*, *sulphate*, and *acetate* are described.

*Anisyl-p-aminophenol*, m. p.  $102-103^{\circ}$ , is prepared in an analogous way from anisylidene-*p*-aminophenol; its *sodium* derivative separates in glistening, golden scales.

*Salicyl-p-aminophenol* has m. p.  $122-123^{\circ}$ .

F. M. G. M.

**Intramolecular Changes of Acylated Compounds.** KARL AUWERS and FRITZ EISENLOHR (*Annalen*, 1909, 369, 209—245. Compare this vol., i, 222, 436).—It has been shown that the transformation  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OAc} \rightarrow \text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , which occurs during the reduction of the corresponding nitro-*O*-acetate, does not always take place at once; in fact, the labile *O*-ester has been isolated in a few cases. It seemed probable, therefore, that the *O*-esters which have not been isolated are also capable of existing for a definite interval of time, but the velocity of transformation into the isomeric *N*-ester is so great as to render their separation impracticable. It should be possible, however, to prevent the migration of the acyl group by causing the amino-group to take part in an intermolecular reaction proceeding with a velocity greater than that of the intramolecular transformation of the *O*-acyl compound. That this is possible follows from the fact that *o*-nitro-*p*-tolyl benzoate when boiled with glacial acetic acid, acetic anhydride, and zinc dust yields *o*-acetyl-amino-*p*-tolyl benzoate. The observation that the latter substance when treated with a dilute alcoholic solution of sodium hydroxide yields *o*-benzoylamino-*p*-cresol, led to the study of the behaviour of mixed esters of amino-phenols when hydrolysed cautiously. A displacement of one acyl group by another does not take place when mixed esters of *m*- and *p*-aminophenols are hydrolysed; only the radicle attached to oxygen is eliminated. In the case of *o*-aminophenol derivatives, however, the radicle attached to nitrogen is displaced by that joined to oxygen provided the latter is much heavier than the former.

The action of alkali on *p*-benzoquinonebenzoylphenylhydrazone has also been investigated (compare Willstätter and Veraguth, *Abstr.*, 1907, i, 453). When a cold dilute alcoholic solution of this substance (1 mol.) is treated with a *N*/10-solution of sodium hydroxide (0.1 mol.), it yields benzeneazophenyl benzoate, although occasionally, for some unknown reason, this reaction does not take place; a one-hundredth molecular proportion of sodium hydroxide does not produce this change. The action of hot aqueous sodium hydroxide on *p*-benzoquinonebenzoylphenylhydrazone is remarkable, in that only small quantities of benzeneazophenol and benzoic acid and relatively large quantities of benzanilide are produced; a true explanation of the formation of the latter substance cannot yet be given.

The transformation of *p*-benzoquinonebenzoylphenylhydrazone into benzeneazophenyl benzoate cannot be effected by boiling with

toluene, xylene, or pyridine. The hydrazone is hydrolysed quantitatively by hot glacial acetic acid, yielding benzeneazophenol; the benzoyl group must be eliminated during its migration from the nitrogen to the oxygen, since benzeneazophenyl benzoate is not affected by boiling glacial acetic acid.

Benzeneazophenyl benzoate is decomposed very slowly when boiled with alcohol, acetic acid, and zinc, although the formation of aniline may be detected soon after the commencement of the experiment. The benzoyl- and acetyl-phenylhydrazones of *p*-benzoquinone when treated in the same manner do not yield even traces of aniline, a fact in accord with the work of Auwers and Eckhardt (Abstr., 1908, i, 480) and of Auwers and Hirt (Abstr., 1908, i, 438).

A solution of *p*-benzoquinonebenzoylphenylhydrazone in acetone, when treated with zinc dust and acetic acid, yields a substance which crystallises in small, colourless crystals, m. p. 137—140°.

*o*-Amino-*p*-cresol is obtained in quantitative yield by the electrolytic reduction of *o*-nitro-*p*-cresol; the diacetyl derivative,  $C_{11}H_{13}O_3N$ , crystallises in large leaflets and flat needles, m. p. 145°. *o*-Benzoylamino-*p*-tolyl acetate,  $C_{16}H_{15}O_3N$ , prepared by the action of acetyl chloride (5 mols.) on *o*-benzoylamino-*p*-cresol (1 mol.) in pyridine, forms pearly leaflets and flat needles, m. p. 134°.

*o*-Acetylamino-*p*-tolyl benzoate,  $C_{16}H_{15}O_3N$ , is most readily prepared by the action of an ethereal solution of benzoyl chloride on sodium *o*-acetylamino-*p*-tolyl oxide in the presence of anhydrous potassium carbonate; it forms colourless needles and compact prisms, m. p. 146°, and is converted by (1) boiling acetic anhydride into the diacetylbenzoyl derivative,  $OAc \cdot C_6H_3Me \cdot NAcBz$ , m. p. 101—102°, and (2) an alcoholic solution of an equivalent quantity of sodium hydroxide into *o*-benzoylamino-*p*-cresol.

*o*-Propionylamino-*p*-cresol,  $C_{10}H_{13}O_3N$ , crystallises in small, glistening, white needles, m. p. 95—96°; the propionate,  $C_{13}H_{17}O_3N$ , forms slender, colourless, pearly leaflets, m. p. 91—92°. *o*-Acetylamino-*p*-tolyl propionate,  $C_{12}H_{15}O_3N$ , crystallises in flat, white needles, m. p. 104—105°, and is converted to a small extent by an alcoholic solution of an equivalent quantity of sodium hydroxide into *o*-propionylamino-*p*-cresol.

*o*-Valerylamino-*p*-cresol,  $C_{12}H_{17}O_3N$ , crystallises in small, slender needles, m. p. 106°; the benzoate,  $C_{19}H_{21}O_3N$ , forms long, slender needles, and softens at 128°, m. p. 142°; when treated with a dilute alcoholic solution of sodium hydroxide, it yields a mixture of *o*-valerylamino-*p*-cresol (9 parts), and *o*-benzoylamino-*p*-cresol (1 part).

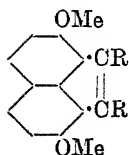
*o*-Heptylamino-*p*-cresol,  $C_{14}H_{21}O_3N$ , forms colourless crystals, m. p. 103—104°; the benzoate,  $C_{21}H_{25}O_3N$ , forms very small crystals, m. p. 87—89°, and when treated with alcoholic sodium hydroxide yields *o*-heptylamino-*p*-cresol.

*o*-Benzoyloxybenzylacetamide  $OBz \cdot C_6H_4 \cdot CH_2 \cdot NHAc$ , forms colourless crystals, m. p. 108—109°. 3:5-Dibromo-2-benzoyloxybenzylacetanilide,  $OBz \cdot C_6H_3Br_2 \cdot CH_2 \cdot NPhAc$ , crystallises in glistening prisms, m. p. 147°. 3:5-Dibromo-2-benzoyloxybenzyl-*p*-nitroacetanilide,  $OBz \cdot C_6H_3Br_2 \cdot CH_2 \cdot NAc \cdot C_6H_4 \cdot NO_2$ , is a faintly yellow, crystal-

line substance, m. p. 153·5—154°. *o*-Benzoyloxybenzaldehydeacetylphenylhydrazone,  $\text{OBz} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{N} \cdot \text{AcPh}$ , crystallises in white needles, m. p. 128°. The four substances just described are hydrolysed by sodium hydroxide solution with elimination of the benzoyl group.

W. H. G.

2:7-Dimethoxy-9:10-diphenylacenaphthylene and the Corresponding Dianisyl Compounds. ERICH BESCHKE [with O. BEITLER and S. STRUM] (*Annalen*, 1909, 369, 184—208).—An investigation on the chemical behaviour of substituted acenaphthylenes having the annexed general formula; the preparation of these substances has been described (this vol., i, 961).



2:7-Dimethoxy-1:8-dibenzoylnaphthalene,  $\text{C}_{28}\text{H}_{20}\text{O}_4$ , is prepared by oxidising a solution of 2:7-dimethoxy-9:10-diphenylacenaphthylene in acetic acid with chromic acid or lead peroxide; it crystallises in colourless, slender needles, m. p. 257°, and is reduced by zinc dust and an alcoholic solution of potassium hydroxide to 2:7-dimethoxy-9:10-diphenylacenaphthene glycol,  $\text{C}_{26}\text{H}_{22}\text{O}_4$ , crystallising in colourless, slender needles, m. p. 188—189°. The latter substance in hot glacial acetic acid is converted by concentrated hydrochloric acid into 2:7-dimethoxy-9:9-diphenylacenaphthenone,

$\text{C}_{10}\text{H}_4(\text{OMe})_2 \begin{smallmatrix} \text{CO} \\ | \\ \text{CPh}_2 \end{smallmatrix}$ ; the same substance is formed by treating 1:8-dibenzoyl-2:7-dimethoxynaphthalene with zinc dust and strong acetic acid, also by oxidising 2:7-dimethoxy-9:10-diphenylacenaphthylene with bromine or concentrated nitric acid in glacial acetic acid; it crystallises in long, pale yellow needles, m. p. 224°, and, when boiled with a 10% alcoholic solution of potassium hydroxide, yields an isomeric substance,  $\text{C}_{26}\text{H}_{20}\text{O}_3$ , crystallising in long, pale yellow needles, m. p. 200°. Either of these isomerides is converted by a 10% alcoholic solution of potassium hydroxide under pressure at 130—140° into 2-hydroxy-7-methoxy-9:9-diphenylacenaphthenone,

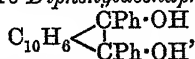
$\text{C}_{25}\text{H}_{18}\text{O}_3$ , crystallising in yellow needles, m. p. 237—238°; the benzoate,

$\text{C}_{32}\text{H}_{22}\text{O}_4$ , forms long needles, m. p. 232—233°.

The following compounds are prepared by the same methods from 2:7-dimethoxy-9:10-di-*p*-anisylacenaphthylene: 2:7-dimethoxy-1:8-di-*p*-methoxybenzoylnaphthalene,  $\text{C}_{28}\text{H}_{24}\text{O}_6$ , colourless needles, m. p. 206—207°; 2:7-dimethoxy-9:10-di-*p*-anisylacenaphthene glycol,

$\text{C}_{28}\text{H}_{26}\text{O}_6$ , colourless, slender needles, m. p. 157°; 2:7-dimethoxy-9:9-di-*p*-anisylacenaphthenone,  $\text{C}_{28}\text{H}_{24}\text{O}_5$ , pale yellow prisms, m. p. 177°.

[With M. KITAJ.]—9:10-Diphenylacenaphthene glycol,



prepared by the action of magnesium phenyl bromide on acenaphthene quinone in ethereal solution, crystallises in small, colourless needles, m. p. 155—156°, and is oxidised by chromic acid in glacial acetic acid, yielding 1:8-dibenzoylnaphthalene,  $\text{C}_{24}\text{H}_{16}\text{O}_3$ , which forms colour-

less, lancet-like crystals, m. p. 189—190°. The glycol, when boiled with glacial acetic acid and concentrated hydrochloric acid, yields

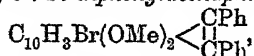
9:9-diphenylacenaphthenone,  $C_{10}H_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CPh}_2 \end{smallmatrix}$ , which forms almost colourless crystals, m. p. 174°, and is converted by a boiling 10% solution of potassium hydroxide in 90% alcohol into 8-diphenylmethylnaphthalene-1-carboxylic acid,  $C_{10}H_6 \begin{smallmatrix} \text{CHPh}_2 \\ \diagup \quad \diagdown \\ \text{CO}_2\text{H} \end{smallmatrix}$ , colourless needles, m. p. 225—226°.

2:7-Dimethoxy-9:10-diphenylacenaphthene,  $C_{10}H_4(\text{OMe})_2 \begin{smallmatrix} \text{CHPh} \\ \diagup \quad \diagdown \\ \text{CHPh} \end{smallmatrix}$ ,

prepared by heating an alcoholic solution of the corresponding acenaphthylene with acetic acid and sodium amalgam, crystallises in colourless needles, m. p. 165°. In the absence of acetic acid, 7-methoxy-9:10-diphenyl-3:4-dihydroacenaphthene,  $C_{25}H_{22}O$ , is formed; it crystallises in colourless needles, m. p. 159°, forms an additive product with 2 atoms of bromine, and, when boiled with amyl alcohol and sodium, yields 7-methoxy-9:10-diphenyl-1:2:3:4-tetrahydroacenaphthene,  $C_{25}H_{24}O$ , which forms colourless, slender needles, m. p. 165°.

2:7-Dimethoxy-9:10-di-p-anisylacenaphthene,  $C_{28}H_{26}O_4$ , prepared in the same way as the analogous phenyl compound, forms colourless, slender needles, m. p. 150°. 7-Methoxy-9:10-di-p-anisyl-4:9-dihydroacenaphthylene,  $C_{27}H_{24}O_3$ , prepared by treating a hot alcoholic solution of 2:7-dimethoxy-9:10-di-p-anisylacenaphthylene with sodium amalgam, crystallises in glistening, bright yellow leaflets, m. p. 191—192°; when reduced with amyl alcohol and sodium, it yields 7-methoxy-9:10-di-p-anisyl-1:2:3:4-tetrahydroacenaphthene,  $C_{27}H_{26}O_3$ , crystallising in felted, white needles, m. p. 133—134°.

Bromo-2:7-dimethoxy-9:10-diphenylacenaphthylene,



prepared by the action of bromine (1 mol.) on a hot solution of the corresponding acenaphthylene in glacial acetic acid, has m. p. 212°; a tribromo-derivative,  $C_{26}H_{11}O_2\text{Br}_3$ , is formed when excess of bromine is used; it crystallises in brick-red needles, m. p. 205°. The bromo-derivative is oxidised by chromic acid in glacial acetic acid to the corresponding diketone,  $C_{26}H_{19}O_4\text{Br}$ , colourless crystals, m. p. 162°.

W. H. G.

**Synthesis of 3:4:8-Trihydroxyphenanthrene Derivatives.** LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1909, 42, 3497—3503. Compare Abstr., 1907, i, 547, 789).—During the conversion of codeine into  $\psi$ -codeine, a wandering of the alcoholic hydroxyl group from position 6 to 8 occurs, and a like change occurs during the conversion of thebaine into thebenine. Attempts have been made to synthesise these compounds in order to prove the validity of these conclusions, but so far without success. The starting point of the work was to prepare 5-bromo-2-methoxybenzyl alcohol,  $C_8H_9O_2\text{Br}$ , from bromosaligenin (Auwers and Büttner, Abstr., 1899, i, 36), potassium hydroxide, and methyl iodide in methyl

alcohol; it crystallises in slender needles, m. p. 75°. This, on treatment with phosphorus pentachloride, yields 5-bromo-2-methoxybenzyl chloride as an oil, and by boiling an alcoholic solution of the chloride with potassium cyanide for five hours, the corresponding nitrile,  $C_9H_5ONBr$ , is obtained in almost colourless needles, m. p. 65°. Hydrolysis of the nitrile with potassium hydroxide leads to the formation of 5-bromo-2-methoxyphenylacetic acid,  $C_9H_9O_3Br$ , which crystallises in needles, m. p. 135°. The sodium salt when heated with o-nitrovanillin methyl ether and acetic anhydride in a sealed tube at 100–110° for twenty-four hours yields 2-nitro-3:4-dimethoxy- $\alpha$ -(5-bromo-2-methoxyphenyl)cinnamic acid,  $C_{18}H_{16}O_7NBr$ , m. p. 208°. The ammonium salt,  $C_{18}H_{19}O_7N_3Br$ , is sparingly soluble, and serves for the separation of the acid from the bromonitrotrimethoxystilbene,  $C_{17}H_{11}O_5NBr$ , which is also formed; it crystallises in yellow rhombohedra, m. p. 136–138°. Reduction of the nitro-acid by ferrous sulphate and ammonia yields the corresponding amino-acid in an 80% yield. It forms yellow flakes.

The sodium salt of this acid, after treatment with sodium nitrite and sulphuric acid, gives, on warming, 5-bromo-3:4:8-trimethoxyphenanthrene-9-carboxylic acid,  $C_{18}H_{15}O_5Br$ ; it crystallises from alcohol in rectangular leaflets, decomp. about 230°; the methyl ester,  $C_{19}H_{17}O_5Br$ , has m. p. 132°.

Neither the ethereal solution of this ester nor the other bromo-compounds described above, react with magnesium. W. R.

Phenyl-o-tolylcarbinol. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1116–1117. Compare this vol., i, 778).—Phenyl-o-tolylcarbinol,  $C_6H_4Me \cdot CHPh \cdot OH$ , prepared by the action of benzaldehyde on the organo-magnesium compound obtained from o-bromotoluene and magnesium, forms well developed prisms, m. p. 95°, and on distillation decomposes apparently into a mixture of phenyl-tolylmethane and phenyl tollyl ketone. With concentrated sulphuric acid, it forms a bright red solution. T. H. P.

Abnormal Behaviour of Asarylaldehyde. TIBOR SZÉKI (*Reprint from Naturw. Museumshften*, 1909, 4, Part I, 1–7).—It has been found previously (Fabinyi and Széki, *Abstr.*, 1906, i, 424) that asarylaldehyde reacts with some magnesium alkyl haloids to form complex ethers, instead of the expected secondary alcohols. In the present paper it is shown that this peculiarity is not exhibited with all magnesium alkyl haloids, but that with certain of these substances, the reaction proceeds normally.

Asarylaldehyde reacts with magnesium anisyl iodide to form p-methoxyphenyl-2:4:5-trimethoxyphenylcarbinol (anisylasarylcarbinol),  $HO \cdot CH(C_6H_4 \cdot OMe) \cdot C_6H_2(OMe)_3$ , m. p. 90°, which forms colourless crystals from hot alcohol and dissolves in sulphuric acid with a red coloration. Magnesium p-tolyl bromide reacts with the aldehyde to give 2:4:5-trimethoxyphenyl-p-tolylmethyl ether,

$O[CH(C_6H_4Me) \cdot C_6H_2(OMe)_3]_2$ , m. p. 175°, which crystallises from a mixture of benzene and light petroleum, and gives a deep red coloration with sulphuric acid. By

condensation with magnesium *o*-tolyl bromide, no crystalline product could be obtained by the ordinary procedure, but by heating the components suspended in a mixture of benzene and light petroleum during three hours, a colourless, crystalline substance, m. p. 85°, having the empirical formula  $C_{33}H_{32}O_5$ , was obtained.

With magnesium  $\alpha$ -naphthyl bromide and asarylaldehyde, 2:4:5-trimethoxyphenyl- $\alpha$ -naphthylcarbinol, m. p. 132°, was obtained. This gives a bluish-violet coloration with sulphuric acid. Magnesium propyl iodide condenses with the aldehyde to form 2:4:5-trimethoxyphenylpropylcarbinol, m. p. 84°, which separates from benzene in colourless crystals, and dissolves in sulphuric acid with a yellow coloration. Magnesium isobutyl iodide, on the contrary, reacts with the aldehyde analogously to magnesium ethyl iodide (*loc. cit.*), and gives  $\delta$ -di-2:4:5-trimethoxyphenyl- $\beta$ -dimethyl- $\Delta^7$ -octene,

$CHMe_2 \cdot CH_2 \cdot CH[C_6H_2(OMe)_3] \cdot C[C_6H_2(OMe)_3] : CH \cdot CHMe_2$ , m. p. 81°, which crystallises from alcohol in colourless needles, and dissolves in sulphuric acid with an orange-red colour. T. A. H.

**Cholesterol. XII.** ADOLF WINDAUS (*Ber.*, 1909, 42, 3770—3775. Compare Abstr., 1908, i, 264, 728).—By oxidising cholesterol with potassium hypobromite, and further oxidising the product with permanganate, a saturated diketotetracarboxylic acid,  $C_{27}H_{40}O_8$ , was obtained. The author now finds that further oxidation of this acid with potassium hypobromite results in the formation of a *monoketotricarboxylic acid*,  $C_{26}H_{40}O_7$ , which is intermediate between the original acid and the tricarboxylic acid,  $C_{25}H_{40}O_6$ , obtained when chromic acid is employed. The new acid is a colourless, amorphous substance, which yields, however, a *potassium hydrogen salt*,  $C_{26}H_{39}O_7K$ , crystallising in four-sided laminae. The acid regenerated from this salt was not crystalline, but gave satisfactory analyses. It does not react with hydroxylamine, but chromic acid readily converts it into the tricarboxylic acid,  $C_{25}H_{40}O_6$ .

The tricarboxylic acid,  $C_{25}H_{40}O_6$ , is further oxidised by hot chromic acid (in acetic acid), with production of traces of an odoriferous substance, already noticed by other observers, acetone, and a new *tetracarboxylic acid*,  $C_{22}H_{32}O_8$ . The yield of this acid is only 8—10%. It crystallises in rosettes of prisms with  $1H_2O$ , and has m. p. 194° (softens 190°). The *rubidium hydrogen salt*,  $C_{22}H_{31}O_8Rb$ , and a similar *caesium hydrogen salt* were prepared and analysed. The acid is stable towards chromic acid, concentrated nitric acid, potassium permanganate, and ozone. It is suggested that the odoriferous substance previously mentioned may be methyl isoamyl ketone. R. V. S.

**Liquid Crystals of Compounds of Cholesterol and Ergosterol with Carbamide.** PAUL GAUBERT (*Compt. rend.*, 1909, 149, 608—610. Compare Abstr., 1908, i, 882).—On heating cholesterol on a glass slip with a carbamide, or an alkyl- or thio-carbamide, interaction occurs in a few seconds with formation of anisotropic liquid substances which solidify on cooling. The liquid crystals in the case of thiocarbamide, thiosinamine, and phenylthiocarbamide are lozenge-shaped, whereas carbamide and the alkylcarbamides give spherulites or birefringent liquid drops. On solidifying, bundles of

crystals or very irregular spherulites are formed. The monobenzyl carbamide of cholesterol is remarkable on account of the large size and uniformity of its solid spherulites, the fineness of the fibres, and the variation of its birefringence with temperature. With the thiocarbamides the optic axis of the lozenge-shaped liquid crystals, which are uniaxial, is perpendicular to the glass slip. Crystals differently oriented appear to dissolve again.

With carbamide, on cooling the isotropic liquid very small spherulites with a dark cross are produced. These coalesce together to form individuals as large as 0.1 mm. in diameter, showing beautiful polarisation tints in concentric circles.

Superfusion was only noticed in the compound of thiosinamine which can be completely solidified at the ordinary temperature without modification of the liquid crystals. True crystallisation is obtained in this substance by reheating.

Ergosterol yields compounds with the carbamides exhibiting the same peculiarity as the cholesterol compounds, but having in general a higher melting point.

R. J. C.

**Preparation of *iso*Propyl *p*-Aminobenzoate.** FARBENFABRIKEN VORM F. BAYER & Co. (D.R.-P. 211801).—When *p*-aminobenzoic acid (or its salts) is treated with *isopropyl* alcohol or iodide, products of therapeutic value are obtained.

*iso*Propyl *p*-aminobenzoate, m. p. 85—86°, is prepared by saturating a moist *isopropyl*-alcoholic solution of *p*-aminobenzoic acid with hydrogen chloride, and heating for several hours at 100°, or by heating *p*-aminobenzoic acid (42 parts), sodium (7 parts), and *isopropyl* alcohol (500 parts) with *isopropyl* iodide (50 parts) during twenty hours; the sulphate crystallises in leaflets.

*iso*Propyl *p*-nitrobenzoate, m. p. 110—111°, dark yellow needles, is prepared in the same way from *p*-nitrobenzoic acid; on reduction with aluminium and moist ether, or with tin and alcoholic hydrochloric acid, the foregoing compound is obtained.

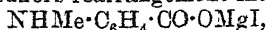
*iso*Propyl *p*- $\beta$ -naphtholazobenzoate,  $\text{CO}_2\text{Pr}^i \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , m. p. 169°, red needles, is prepared by the esterification of *p*- $\beta$ -naphtholazobenzoic acid.

F. M. G. M.

**Synthesis of Aromatic Amino-acids by Rearrangement.** II. JOSEF HOUBEN and ARNOLD SCHOTTMÜLLER (*Ber.*, 1909, 42, 3729—3750).—The authors have continued their attempts to effect the transference of a carboxyl group from the nitrogen atom to the nucleus in aromatic amino-compounds. The *p*-methylaminobenzoic acid mentioned in a former paper (*Abstr.*, 1904, i, 1014) has been found to consist mainly of *p*-dimethylaminobenzoic acid. When sodium phenylacetylcarbamate (from sodioacetanilide and carbon dioxide) is heated, only sodium malonate is formed. The corresponding derivative of formanilide yields similarly sodium oxanilate, whilst sodium phenylbenzoylcarbamate (from sodiobenzanilide) loses carbon dioxide when heated. Experiments with the sodium derivatives of the aromatic amines (compare Titherley, *Trans.*, 1897, 71, 462) were also unsuccessful. Magnesium iodide phenylmethylcarbamate when heated in a sealed tube is converted into *p*-dimethylaminobenzoic acid. When

the rearrangement is effected by heating in a stream of carbon dioxide in dimethylaniline solution, the same acid is produced, but the yield is much better (40%). If saffrole or quinoline is employed as solvent, secondary products are obtained. When, instead of dimethylaniline, methylaniline is employed, it participates in the reaction :

$\text{NHMePh} + \text{Mg} + \text{CH}_3\text{I} + \text{CO}_2 = \text{CH}_3 + \text{NMePh} \cdot \text{CO} \cdot \text{OMgI}$ ,  
and the product then suffers rearrangement into



an almost quantitative yield of *p*-monomethylaminobenzoic acid being obtained. The methylaniline may be replaced by a mixture of aniline and dimethylaniline, and dimethylaniline hydriodide may be used instead of a mixture of methylaniline and methyl iodide. *Dimethylaniline hydriodide* has m. p. 150°.

Methylation of *p*-aminobenzoic acid with methyl sulphate in aqueous alcohol yielded a mixture of products from which *p*-dimethylaminobenzoic acid was isolated. Methylation in glacial acetic acid (compare Houben and Brassert, Abstr., 1906, i, 845) gave a considerable quantity of *p*-aminobenzoic acid sulphate. On treating the mother liquor with sodium nitrite, a nitroso-compound was obtained, which had m. p. 202—203°. It gave an ammonium salt, which was golden-yellow in colour and seemed to have m. p. 215—217°, and when decomposed with dilute acetic acid yielded pure *p*-methylnitrosoaminobenzoic acid.

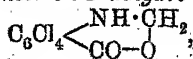
[With WALTER BRASSETT.]—On digesting this acid with alcoholic hydrogen chloride at the ordinary temperature, the nitroso-group is eliminated and *ethyl p*-methylaminobenzoate hydrochloride is obtained. When treated with sodium nitrite, this yields *ethyl p*-methylnitrosoaminobenzoate, which crystallises in groups of needles, and has m. p. 57°. *p*-Methylaminobenzoic acid forms brush-like clusters of needles, and has m. p. 160° (decomp.); its *ethyl* ester has m. p. 65—67°.

*Magnesium iodide phenylethylcarbamate* was prepared in ether, and was then heated in a current of carbon dioxide at 200°. The main product had m. p. 195°, and was found to be *p*-methyl ethylaminobenzoic acid. By nitrosylating the mother liquor, *p*-ethylnitrosoaminobenzoic acid was obtained. The other methods mentioned above were applied to similar reactions with ethylaniline and diethylaniline.

R. V. S.

**Tetrachloroanthranilic Acid.** VICTOR VILLIGER and LOUIS BLANGNEY (*Ber.*, 1909, 42, 3549—3552. Compare Tust, Abstr., 1887, 1046; 1888, 836).—This acid can be obtained in a crystalline condition from tetrachlorophthalic anhydride by first converting it into the acid amide by treatment with ammonia, which then, when treated with sodium hypochlorite and sodium hydroxide, yields the tetrachloroanthranilic acid; this crystallises from alcohol in long needles, m. p. 182—183°. It is a strong acid and yields well characterised salts, and, on heating above its m. p., is decomposed quantitatively into 2:3:4:5-tetrachloroaniline. Tust's acid was probably impure.

5:6:7:8-Tetrachloro-1-keto-3:4-dihydro-2:4-benzoxazine,



obtained by the condensation of the acid with formaldehyde, crystallises in leaflets, m. p. 216°. Hot sodium carbonate regenerates the acid, and potassium cyanide yields tetrachloro-*o*-cyanomethylanthranilic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{Cl}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$ , needles, m. p. 178°.

Tetrachloroaniline has m. p. 121° (Beilstein and Kurbatoff, Abstr., 1879, 143, give 118°). W. R.

**Preparation of *o*-Alkylthiolbenzoic Acids and their Derivatives.** FARBERWERKE VORM MEISTER, LUCIUS & BRÜNING (D.R.-P. 211679. Compare Abstr., 1908, i, 648, 797; this vol., i, 231).—It has now been found that in the preparation of *o*-alkylthiolbenzoic acids it is not necessary to start from thiolbenzoic acid itself, but the more accessible *o*-xanthylbenzoic acid may be used. This on methylation yields methyl *o*-methylthiolbenzoate. *o*-Methylthiolbenzoic acid is obtained when *o*-diazobenzoic acid is heated successively with potassium xanthate at 70–80° and sodium methyl sulphate in alkaline solution at 100–120°. When methylanthranilate is employed, methyl *o*-xanthylbenzoate,  $\text{OEt}\cdot\text{CS}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , a pale brown oil, is obtained; this on treatment with alkaline sodium alkyl sulphate is converted into the corresponding alkylthiolbenzoate. F. M. G. M.

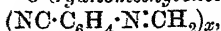
**Nitrile Oxides. IV. Relations of Nitrile Oxides to the Reactions of Hoffmann and Curtius.** HEINRICH WIELAND (*Ber.*, 1909, 42, 4207–4209).—The author has shown (this vol., i, 216) that, when heated in indifferent solvents, the nitrile oxides undergo rearrangement to the isomeric carbimides:  $\text{O} \begin{smallmatrix} \text{CR} \\ | \\ \text{N} \end{smallmatrix} \rightarrow \text{R}\cdot\text{N}\cdot\text{C}\cdot\text{O}$ . The

assumption that, when the polymeric nitrile oxides, the probable constitution of which has been already given (*loc. cit.*), undergo this change, they are first de-polymerised to the simple nitrile oxides, is supported by the observation that benzonitrile oxide is converted partly into phenylcarbimide when heated in xylene solution. In this case, however, this change does not proceed readily, since before the temperature (about 110°) at which the isomeric change occurs is reached, the more favoured polymerisation to diphenylfuroxan takes place; this reaction is not, however, observed with the tri-nitrile oxides, for which the conditions of spontaneous decomposition into simple molecules are also those of the isomeric change.

Unsuccessful attempts were made to obtain benzonitrile oxide: (1) by the removal of hydrogen bromide from benzoylbromamide, which forms the first product of the action of hypobromite on benzamide, and (2) by the removal of nitrogen from benzoylazoimide. The author, therefore, agrees with Schroeter (this vol., i, 617) that the nitrile oxides do not stand in causal relation either with Hoffmann's reaction or with Curtius' azoimide reaction (this vol., i, 216). T. H. P.

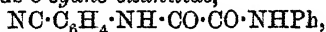
***o*-Aminobenzonitrile.** ARNOLD REISSERT and F. GRUBE (*Ber.*, 1909, 42, 3710–3721).—Numerous experiments have been made on the reduction of *o*-nitrobenzonitrile in the hope of obtaining *o*-cyanophenylhydroxylamine, but they have yielded only the reduction

products previously known. For the preparation of *o*-aminobenzonitrile, the authors revert to stannous chloride, by means of which a yield of 80% is obtained. *o*-Cyanomethyleneaniline,



from *o*-aminobenzonitrile (dissolved in acetone) and formaldehyde solution, serves to identify the nitrile; it forms needles, m. p. 211—212°.

*Di-o-cyanoxanilide*,  $\text{NC}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$ , is obtained on heating equal weights of *o*-aminobenzonitrile and methyl oxalate at 140—150°; it crystallises in almost colourless, slender needles, m. p. 318° (decomp.). When warmed with alcoholic potassium hydroxide or concentrated sulphuric acid, the compound is hydrolysed; on long-continued boiling with aqueous alkali, 4-hydroquinazolone-2-carboxylic acid (see below) is produced in small amount. When *o*-aminobenzonitrile is heated for three hours in a reflux apparatus with three times its weight of methyl oxalate, *methyl o-cyanoxanilate*,  $\text{NC}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}_2\text{Me}$ , is produced; it crystallises in long, colourless needles of m. p. 139°, and is hydrolysed on boiling with water. With aniline it yields *o-cyano-oxanilide*,



which forms pale yellow needles, m. p. 197·5°. *o*-Cyano-oxanilic acid forms long, silky needles, m. p. 126°; when boiled with water it decomposes into the nitrile and oxalic acid. When kept at the ordinary temperature in dilute acid solution, it changes into an isomeric acid which is identical with the 4-hydroquinazolone-

2-carboxylic acid,  $\text{C}_6\text{H}_4\cdot\begin{matrix} \text{CO}\cdot\text{NH} \\ | \\ \text{N}=\text{C}\cdot\text{CO}_2\text{H} \end{matrix}$  or 4-hydroxyquinazoline-

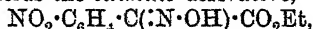
2-carboxylic acid,  $\text{C}_6\text{H}_4\cdot\begin{matrix} \text{C}(\text{OH})\cdot\text{N} \\ | \\ \text{N}=\text{C}\cdot\text{CO}_2\text{H} \end{matrix}$ , first prepared by Griess.

Diazotisation of the nitrile and subsequent reduction did not yield *o*-cyanophenylhydrazine as expected, but the isomeric 3-aminoindazole of m. p. 153—154° (Bamberger and Goldberger, Abstr., 1899, i, 545).

*o*-Aminothiobenzamide,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CS}\cdot\text{NH}_2$ , is prepared by dissolving *o*-aminobenzonitrile in alcohol, adding aqueous 25% ammonia, and then passing hydrogen sulphide. The compound crystallises in plates with serrated edges, has m. p. 121·5° (sinters previously), and is not changed at 200°, thus differing from the *m*-compound. The *hydrochloride* decomposes at 203°. The *ortho*-compound reacts with an alcoholic solution of iodine analogously to the *meta*-compound (Wanstrat, Ber., 1873, 6, 333), the *hydriodide* of the base,  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$ , being produced. It forms long, lanceolate crystals, which have m. p. 197—198° (decomp.). The salt is remarkably stable towards cold alkali. The base,  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$ , liberated by means of silver oxide, forms colourless needles, which have m. p. 170° (sintering previously). The *hydrochloride*,  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}\cdot 2\text{HCl}$ , has m. p. 118°; from it the base is easily set free by alkali. The *nitrate*,  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}\cdot 2\text{HNO}_3$ , decomposes at 175°. The *sulphate*,  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}\cdot \text{H}_2\text{SO}_4$ , has m. p. 210°. The *platinichloride*,  $[\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}]\cdot \text{H}_2\text{PtCl}_6$ , and the *mercurichloride* (decomposing at 223°) were also prepared. Diazotisation of *o*-aminothiobenzamide in strongly acid solution yields 4-thiol-

1:2:3-benzotriazine,  $C_6H_4 \begin{smallmatrix} C(SH):N \\ N==N \end{smallmatrix}$  (compare Finger, Abstr., 1888, 948), which crystallises in golden-yellow needles, m. p. 187.5° (decomp.). It gives a *benzoyl* compound, m. p. 163° (decomp.), and an *acetyl* compound,  $C_7H_4N_3SAc$ , m. p. 144° (decomp.). A *methyl* compound,  $C_7H_4N_3SMe$ , is produced when thiolbenzotriazine is heated with a methyl-alcoholic solution of sodium methoxide and a little methyl iodide in a sealed tube at 120°. It forms yellow crystals, m. p. 101–102° (previously sintering). Oxidation with permanganate converts it into 4-hydroxy-1:2:3-benzotriazine, white needles, decomposing at 212–213°. R. V. S.

Reactivity of the Methylene Groups in Ethyl *p*- and *o*-Nitrophenylacetates. WALTHER BORSCHKE (*Ber.*, 1909, 42, 3596–3602. Compare this vol., i, 232).—A 50–60% yield of *p*-nitrophenylacetic acid can be obtained by nitrating a solution of phenylacetic acid in concentrated sulphuric acid with a mixture of concentrated nitric and sulphuric acids. The ethyl ester has b. p. 136–137°/20 mm. A benzoyl derivative could not be obtained by the action of sodium ethoxide and benzoyl chloride on the ester, and although sodium ethoxide and 2:4-dinitrobromobenzene reacted with the ester, only tarry products were obtained. A condensation product with benzenediazonium chloride could not be obtained in either acetic acid or alkaline solution. With amyl nitrite and sodium ethoxide the ester yields the *oximino*-derivative,



and the *oxime* of ethyl *p*-nitrophenylglyoxylate, which crystallises from dilute alcohol in slender needles, m. p. 181–182° (decomp.). The corresponding *acid*,  $C_8H_6O_5N_3$ , crystallises from water in colourless needles, m. p. 160–161° (decomp.). When heated, the acid yields carbon dioxide, water, and *p*-nitrobenzonitrile.

Ethyl *p*-nitrophenylacetate condenses with benzaldehyde in the presence of a few drops of piperidine, yielding a thin, dark brown oil, which, on hydrolysis with sulphuric acid, yields *α-p*-nitrophenylcinnamic acid. When *p*-nitrobenzaldehyde is used, ethyl *α-p*-nitrophenyl-*p*-nitrocinnamate,  $NO_2 \cdot C_6H_4 \cdot CH:C(CO_2Et) \cdot C_6H_4 \cdot NO_2$ , m. p. 164°, is obtained. The corresponding *acid*,  $C_{15}H_{10}O_6N_3$ , forms yellow crystals from ethyl acetate, and has m. p. 264° (decomp.).

*α-p*-Nitrophenylcoumarin (Abstr., 1900, i, 438) can be obtained in a similar manner from the nitro-ester, salicylaldehyde, and piperidine.

Ethyl *o*-nitrophenylacetate is most readily prepared by Reissert's method (*Ber.*, 1897, 30, 1043). It does not react with benzenediazonium chloride or bromo-2:4-dinitrobenzene, but with amyl nitrite and sodium ethoxide yields ethyl *o*-nitro-oximinophenylglyoxylate (Gabriel, Abstr., 1883, 920), but no ethyl benzisoxazole-*α*-carboxylate. The *o*-nitro-ester does not condense with aldehydes as readily as the isomeric *p*-compound.

*α-o*-Nitrophenylcoumarin,  $C_{15}H_8O_4N_2$ , forms pale yellow crystals, begins to sinter at 160°, and has m. p. 215°. Sodium *o*-nitrophenylacetate, benzaldehyde, and acetic anhydride yield *α-o*-nitrophenylcinnamic acid,  $CHPh:C(CO_2H) \cdot C_6H_4 \cdot NO_2$ , m. p. 193°. J. J. S.

**Chlorides of Certain Acylamino-acids.** JULES MAX (*Annalen*, 1909, 369, 276—286).—A number of chlorides of acylamino-acids have been prepared by the action of acetyl chloride and phosphorus pentachloride on acylamino-acids (compare Fischer, *Abstr.*, 1905, i, 263). Certain of the compounds prepared have been described recently by Mohr and Stroschein (this vol., i, 581).

Benzoylalaninyl chloride forms slender, white leaflets, sinters at 125°, m. p. 130° (decomp.); with methyl alcohol it yields *benzoylalanine methyl ester*,  $C_{11}H_{13}O_3N$ , crystallising in small, white, striated rods, m. p. 80·5—81·5° (corr.).

*Benzoyl-leucyl chloride*,  $C_4H_9\cdot CH(NHBz)\cdot COCl$ , crystallises in small needles and decomposes at 80—90°; *benzoyl-leucine methyl ester*,  $C_{14}H_{19}O_3N$ , has m. p. 95—96° (corr.); the *ethyl ester*,  $C_{15}H_{21}O_3N$ , crystallises in cubes and rods, m. p. 73—75°; *benzoyl-leucinamide*,  $C_{18}H_{23}O_3N_2$ , crystallises in glistening, hexagonal, striated plates, m. p. 171° (corr.).

*Benzoylphenylalaninyl chloride*,  $CH_2Ph\cdot CH(NHBz)\cdot COCl$ , forms colourless, rhombic plates, and decomposes at 123—125°; *benzoylphenylalanine methyl ester*,  $C_{17}H_{19}O_3N$ , has m. p. 86·5—87·5° (corr.); the corresponding *ethyl ester*,  $C_{18}H_{21}O_3N$ , forms tufts of small, colourless needles, m. p. 95—95·5° (corr.); *benzoylphenylalaninamide*,  $C_{16}H_{16}O_2N_2$ , crystallises in stellate aggregates of matted needles, m. p. 198° (corr.).

*Benzoylaspartyl chloride*,  $COCl\cdot CH(NHBz)\cdot CH_2\cdot COCl$ , sinters at 100° and decomposes just above this temperature; *methyl benzoylaspartate*,  $CO_2Me\cdot CH(NHBz)\cdot CH_2\cdot CO_2Me$ , crystallises in long, colourless needles, m. p. 94—95° (corr.); the *ethyl ester*,  $C_{15}H_{19}O_5N$ , forms long, glistening needles, m. p. 97—98° (corr.),  $[\alpha]_D^{20} - 23\cdot9^\circ$  (in alcohol); the corresponding *diamide*,  $C_{11}H_{13}O_3N_2$ , turns brown at 250°, m. p. 264° (decomp., corr.).

*Formylglycyl chloride*,  $CHO\cdot NH\cdot CH_2\cdot COCl$ , decomposes at 100°; the analogous *acetyl compound*,  $NHAc\cdot CH_2\cdot COCl$ , crystallises in small plates and decomposes at 115—118°. W. H. G.

**Catalytic Action of Colloidal Metals of the Platinum Group.** VIII. Progressive Reduction of Phenyl Propiolic Acid. CARL PAAL and WILHELM HARTMANN (*Ber.*, 1909, 42, 3930—3939. Compare *Abstr.*, 1908, i, 599; this vol., i, 358, 381, 545).—By the partial reduction of phenylpropiolic acid, by shaking with hydrogen (1 mol.) and palladium hydrosol, *allocinnamic acid* was obtained. In early experiments made in cold weather, the acid, m. p. 42° (*isocinnamic acid*), was obtained, and this is regarded as the primary form. At higher temperatures, Liebermann's *allocinnamic acid*, m. p. 68°, was formed. Subsequently, all experiments, even in the cold, led to the formation of the *allo-acid*. From preparations made in another laboratory, Liebermann's *isocinnamic acid*, m. p. 57—58°, was at first obtained; subsequently here, too, only *allocinnamic acid* could be prepared (compare Büllmann, this vol., i, 155, 382; Liebermann, this vol., i, 155).

Cinnamic acid, m. p. 132—133°, is formed in small quantity during the reduction.

Total reduction of phenylpropionic acid by the same method leads to  $\beta$ -phenylpropionic acid, m. p. 47—48°. E. F. A.

**Influence of Constitution on the Rotatory Power of Optically Active Substances.** HANS RUPE (*Annalen*, 1909, 369, 311—369. Compare Abstr., 1903, i, 565).—An investigation of the effect on the optical rotatory power produced by the introduction of a methyl or phenyl group into the menthyl esters of various acids. The results obtained may be summarised as follows:

(1) The replacement of a methyl by a phenyl group is usually accompanied by a marked decrease in the optical rotatory power; for example, menthyl crotonate has  $[\alpha]_D^{20} - 91.06^\circ$ , whilst menthyl cinnamate has  $[\alpha]_D^{20} - 76.95^\circ$  (compare paragraph 4).

(2) The optical rotatory power is diminished by an assemblage of strong negative groups (phenyl): thus, menthyl cinnamate has  $[\alpha]_D^{20} - 76.95^\circ$ , whilst menthyl  $\beta$ -phenylcinnamate has  $[\alpha]_D^{20} - 37.92^\circ$ .

(3) The optical rotatory power of esters of acids with optically active alcohols is increased by substituting an  $\alpha$ -hydrogen atom by a negative group, whilst it is decreased if the group be introduced at some distance from the  $\alpha$ -carbon atom.

(4) The influence exerted by a phenyl group on the optical rotatory power becomes greater as it becomes more distant from the asymmetric carbon atom ("*Hebelwirkung*"); in this it differs from the ethylene linking, which has but a small effect on the optical rotatory power when greatly removed from the asymmetric carbon atom; for example, the menthyl esters of valeric acid,  $\Delta^8\gamma$ -pentaenoic acid, and  $\Delta^7\delta$ -pentaenoic acid have the values  $[\alpha]_D^{20} - 69.05^\circ$ ,  $-72.51^\circ$ , and  $-67.32^\circ$  respectively, whilst the menthyl esters of propionic acid, phenylacetic acid, butyric acid,  $\beta$ -phenylpropionic acid, hexoic acid, and  $\delta$ -phenylvaleric acid have the values  $[\alpha]_D^{20} - 75.51^\circ$ ,  $-69.57^\circ$  (difference = 6),  $-70.46^\circ$ ,  $-58.48^\circ$  (difference = 12),  $-64.86^\circ$ , and  $-33.86^\circ$  (difference = 31) respectively.

The menthyl esters are prepared by acting on the acid chloride with a solution of menthol and pyridine in benzene; the acid chloride is obtained by treating the dry sodium salt of the acid with a solution of phosphoryl chloride in benzene.

In certain cases the menthyl ester obtained from a racemic acid is the ester of one of the optically active antipodes; for example, menthyl *l*- $\beta$ -phenylbutyrate was obtained from *dl*- $\beta$ -phenylbutyric acid.

[With E. BUSOLT.]—Menthyl cinnamate, prepared from cinnamic acid obtained from storax, is a colourless oil, b. p. 111—112°/0.25 mm.,  $[\alpha]_D^{20} - 76.95^\circ$  (in benzene). Menthyl  $\beta$ -phenylpropionate forms long, white prisms, m. p. 32°, b. p. 197—198°/12 mm.,  $[\alpha]_D^{20} - 58.48^\circ$  (in benzene). Menthyl  $\alpha$ -methylcinnamate forms long, slender, white needles, m. p. 52°,  $[\alpha]_D^{20} - 62.60^\circ$ . Menthyl  $\beta$ -phenyl- $\alpha$ -methylpropionate,  $C_{20}H_{30}O_2$ , forms glistening, white needles, m. p. 41°,  $[\alpha]_D^{20} - 50.73^\circ$ . Menthyl  $\beta$ -methylcinnamate,  $C_{20}H_{28}O_2$ , crystallises in white leaflets, m. p. 82°,  $[\alpha]_D^{20} - 65.89^\circ$ . *l*- $\beta$ -Phenylbutyric acid is a colourless, viscid oil, b. p. 157.25—157.75°/12 mm.,  $[\alpha]_D^{20} - 57.23^\circ$ ; the chloride has b. p. 112—113°/11.5 mm.; the menthyl ester,  $C_{20}H_{30}O_2$ , crystallises in long,

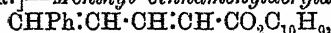
transparent prisms, m. p. 47—48°,  $[\alpha]_D^{20} - 76.26^\circ$ ; the corresponding *d*-compounds could not be obtained in a pure state. *Menthyl α-phenylcinnamate*,  $C_{25}H_{30}O_2$ , forms silvery leaflets, m. p. 81—82°,  $[\alpha]_D^{20} - 53.44^\circ$ . *Menthyl αβ-diphenylpropionate*,  $C_{25}H_{32}O_2$ , forms long, slender, silky needles, m. p. 67—68°,  $[\alpha]_D^{20} - 86.04^\circ$ . *Menthyl β-phenylcinnamate* crystallises in small, glistening, white needles, m. p. 66—67°,  $[\alpha]_D^{20} - 37.92^\circ$ . *Menthyl ββ-diphenylpropionate* forms small, slender, white needles, m. p. 40—41°,  $[\alpha]_D^{20} - 61.72^\circ$ . *Menthyl phenylpropiolate*,  $C_{10}H_{24}O_2$ , forms long, pale yellow needles, m. p. 67°,  $[\alpha]_D^{20} - 71.77^\circ$ .

*Menthyl phenylacetate* has b. p. 94—95°/0.25 mm.,  $[\alpha]_D^{20} - 67.57^\circ$ . *Menthyl atropate (α-phenylacrylate)*,  $C_{19}H_{26}O_2$ , is an unstable, pale yellow, limpid oil, which changes into a viscid, gummy substance when kept,  $[\alpha]_D^{20} - 63.03^\circ$ . *Menthyl α-phenylpropionate*,  $C_{19}H_{28}O_2$ , is a colourless oil, b. p. 90—91°/0.25 mm.,  $[\alpha]_D^{20} - 61.87^\circ$ . *Menthyl methyl-atropate (α-phenylcrotonate)*,  $C_{20}H_{28}O_2$ , is a yellow oil, which decomposes when distilled in a vacuum,  $[\alpha]_D^{20} - 46.13^\circ$  (?). *Menthyl α-phenylbutyrate*,  $C_{20}H_{30}O_2$ , b. p. 112—114°/0.5 mm., could not be obtained quite pure,  $[\alpha]_D^{20} - 26.78^\circ$  (?).

*Menthyl methacrylate*,  $C_{14}H_{24}O_2$ , is a colourless, limpid oil, b. p. 125—126°/14 mm.,  $[\alpha]_D^{20} - 91.76^\circ$ . *Menthyl isobutyrate* has b. p. 116—117°/12 mm.,  $[\alpha]_D^{20} - 72.05^\circ$ . *Menthyl crotonate* has b. p. 134°/11 mm.,  $[\alpha]_D^{20} - 91.06^\circ$ . *Menthyl butyrate* has b. p. 126°/12.5 mm.,  $[\alpha]_D^{20} - 70.56^\circ$ . *Menthyl α-methylcrotonate*,  $C_{15}H_{26}O_2$ , is a colourless, limpid oil, b. p. 140—141°/10.25 mm.,  $[\alpha]_D^{20} - 84.38^\circ$ . *Menthyl α-methylbutyrate*,  $C_{15}H_{26}O_2$ , is a colourless liquid, b. p. 130°/9 mm.,  $[\alpha]_D^{20} - 63.97^\circ$ . *Menthyl β-methylcrotonate* is a slightly yellow liquid, b. p. 144—145°/13 mm.,  $[\alpha]_D^{20} - 88.60^\circ$ . *Menthyl β-methylbutyrate* is a colourless, limpid liquid, b. p. 129°/9 mm.,  $[\alpha]_D^{20} - 64.02^\circ$ .

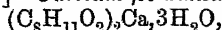
[With P. HÄUSSLER.]—*Menthyl diphenylacetate*,  $C_{24}H_{30}O_2$ , forms small, slender, white needles, m. p. 52—53°,  $[\alpha]_D^{20} - 66.70^\circ$ .

[With F. MÜNTER.]—*Menthyl cinnamethylacrylate*,



is a viscid, gelatinous substance, which commences to decompose in a vacuum at 80°,  $[\alpha]_D^{20} - 75.14^\circ$  (in benzene). *Menthyl δ-phenyl-Δ<sup>8</sup>-pentoate*,  $C_{21}H_{30}O_2$ , is a pale yellow oil, b. p. 217—218°/11.5 mm.,  $[\alpha]_D^{20} - 47.54^\circ$ . *Menthyl δ-phenylvalerate*,  $C_{21}H_{32}O_2$ , is a viscid, pale yellow oil, b. p. 206—207°/11.5 mm.,  $[\alpha]_D^{20} - 33.86^\circ$ .

[With WALTHER LOTZ.]—*Calcium βδ-dimethylsorbate*,



crystallises in tufts of small, white needles; the barium salt ( $2H_2O$ ) forms aggregates of glistening needles; the *menthyl* ester,  $C_{18}H_{30}O_2$ , is a colourless oil, b. p. 183—184°/14 mm.,  $[\alpha]_D^{20} - 59.80^\circ$  (in alcohol). The lactone of *γ-hydroxy-βδ-dimethyl-Δ<sup>α</sup>-hexenoic acid*,  $C_8H_{12}O_2$ , is a colourless, limpid liquid, b. p. 111—113°/14 mm.; the barium and silver salts of the acid were analysed. *βδ-Dimethyl-Δ<sup>β</sup>-hexenoic acid*,  $CHMe_2:CH:CHMe:CH_2:CO_2H$ , is a colourless liquid, b. p. 119.5—120.5°/14 mm.; the cadmium salt ( $2H_2O$ ) forms glistening, white needles; the *menthyl* ester,  $C_{18}H_{32}O_2$ , has b. p. 169—170°/14 mm.,  $[\alpha]_D^{20} - 68.51^\circ$  (in alcohol). *βδ-Dimethylhexoic acid*,  $C_8H_{16}O_2$ , has b. p. 118.5—119.5°/14 mm.; the *menthyl* ester,  $C_{18}H_{34}O_2$ , is a colourless oil, b. p. 168.5—169.5°/14 mm.,  $[\alpha]_D^{20} - 57.38^\circ$ .

[With C. DORSCHKY.]—*Amyl α-phenylcinnamylacrylate*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CO}_2\text{C}_5\text{H}_{11}$ , has b. p.  $170\text{--}172^\circ/0.25$  mm.,  $[\alpha]_D^{20} + 3.87^\circ$  (in alcohol); *amyl α,δ-diphenyl-Δ<sup>2</sup>-pentenolate* and *amyl α,δ-diphenyl-Δ<sup>2</sup>-pentenolate*,  $\text{C}_{22}\text{H}_{26}\text{O}_2$ , are colourless oils, having  $[\alpha]_D^{20} + 7.15^\circ$  and  $+4.84^\circ$  (in alcohol) respectively.

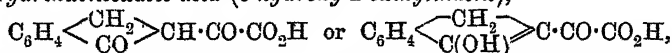
[With C. LIECHTENHAN.]—*α,δ-Diphenylvaleric acid*,  $\text{C}_{17}\text{H}_{18}\text{O}_2$ , crystallises in colourless, hexagonal plates, m. p.  $77\text{--}78^\circ$ ; the *amyl* ester,  $\text{C}_{22}\text{H}_{28}\text{O}_2$ , is a colourless oil with a slight fluorescence, b. p.  $140\text{--}141^\circ/0.5$  mm.,  $[\alpha]_D^{20} + 4.85^\circ$  (in alcohol). W. H. G.

Solubilities of Salicylates of the United States Pharmacopoeia in Aqueous Alcohol Solution at  $25^\circ$ . ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1909, 31, 1164—1168).—A redetermination of the solubility of the salicylates of ammonium, lithium, phenyl, quinine, sodium, strontium, and bismuth, also of free salicylic acid in aqueous alcohol solutions at  $25^\circ$ . The results obtained are tabulated, and curves given in the original. L. DE K.

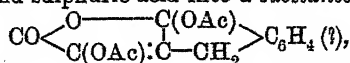
Condensation Products of *o*-Phthalaldehyde. II. JOHANNES THIELE and JOSEF SCHNEIDER (*Annalen*, 1909, 369, 287—299).—Pyruvic acid condenses with *o*-phthalaldehyde in a similar manner to acetone and acetophenone, yielding hydrindoneoxalic acid (compare Thiele and Falk, *Abstr.*, 1906, i, 750). The condensation of methyl ketones with *o*-phthalaldehyde leads not only to the formation of hydrindones, but also of a yellow substance (*loc. cit.*), which is now shown to be *o*-phenylene-ββ-naphthylene ketone (*isochrysoketone*). Ethyl acetonedicarboxylate also condenses with *o*-phthalaldehyde, yielding ethyl benzocycloheptadienonedicarboxylate.

Aniline reacts with *o*-phthalaldehyde, yielding phenylphthalimidine (compare Hessert, *Abstr.*, 1878, 66) or phenylphthalimidinanil, according to the proportions of the reacting substances used.

*Hydrindoneoxalic acid (3-hydroxy-2-oxalylindene)*,

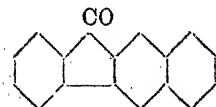


crystallises in silky, pale yellow needles, m. p.  $211\text{--}212^\circ$ ; the *methyl* ester,  $\text{C}_{12}\text{H}_{10}\text{O}_4$ , forms long, white needles, m. p.  $99.5^\circ$ . The acid may also be obtained by the action of potassium hydroxide on a solution of *α*-hydrindone and methyl oxalate in methyl alcohol; it is converted by acetic anhydride and sulphuric acid into a substance,



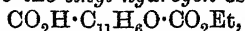
which forms colourless crystals, m. p.  $149\text{--}150^\circ$  (decomp.).

*o*-Phenylene-ββ-naphthylene ketone, annexed formula, prepared by the interaction of *o*-phthalaldehyde and *α*-hydrindone in alcoholic solution in the presence of potassium hydroxide, crystallises in pale yellow needles, m. p.  $152^\circ$ ; the *phenylhydrazone*,  $\text{C}_{23}\text{H}_{16}\text{N}_2$ , forms yellow crystals, m. p.  $174^\circ$ .



*Ethyl benzocycloheptadienonedicarboxylate*,

$C_6H_4 \begin{smallmatrix} \text{CH}:\text{C}(\text{CO}_2\text{Et}) \\ \text{CH}:\text{C}(\text{CO}_2\text{Et}) \end{smallmatrix} > \text{CO}$ , crystallises in colourless leaflets, m. p. 95.5°, and is converted by (1) a dilute methyl-alcoholic solution of potassium hydroxide into the *ethyl hydrogen ester*,



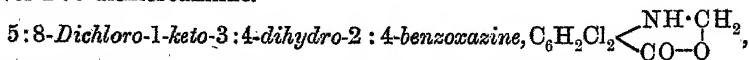
crystallising in small, slender, white needles, m. p. 185°; (2) hot 20% sulphuric acid into the corresponding *acid*,  $C_{13}H_8O_5$ , m. p. 210° (decomp.); (3) an alcoholic solution of phenylhydrazine into the *additive product*,  $C_{23}H_{24}O_5N_2$ , colourless needles, m. p. 138°; the corresponding *dimethyl ester* forms colourless needles, m. p. 181°.

*Benzocycloheptadienonecarboxylic acid*,  $C_{12}H_8O_3$ , is formed when the dicarboxylic acid is heated at its m. p., or when the diethyl ester is boiled with aqueous sodium hydroxide; it crystallises in long, white needles, m. p. 172°.

*Phenylphthalimidinanyl*,  $C_6H_4 \begin{smallmatrix} \text{C}(\text{NPh}) \\ \text{CH}_2 \end{smallmatrix} > \text{NPh}$ , crystallises in colourless needles, turns brown at 135°, m. p. 142—143°; the *platinichloride*,  $C_{40}H_{32}N_4H_2PtCl_6$ , is a reddish-yellow, crystalline powder, m. p. 212—213° (decomp.). W. H. G.

**Dichlorophthalic and Dichloroanthranilic Acids.** VICTOR VILLIGER (*Ber.*, 1909, 42, 3529—3549).—Only two of the four possible dichloro-*o*-phthalic acids have been described, the 3:6-acid by Graebe and Gourevitz (*Abstr.*, 1900, i, 547), and the 3:5-acid by Crossley and Le Sueur (*Trans.*, 1902, 81, 1533). Neither of these acids was prepared by the direct chlorination of the phthalic acid. If, however, phthalic anhydride is dissolved in fuming sulphuric acid (23%  $\text{SO}_3$ ) and chlorine is passed into the liquid, iodine being used as the carrier, the following reaction occurs:  $C_8H_4O_3 + 2Cl_2 + 2SO_3 = C_8H_2O_3Cl_2 + 2ClSO_3H$ , so that the reaction can be controlled by weighing. The reaction is finished after forty hours at 40—60°. The chlorinated anhydride is obtained as a white, crystalline powder by pouring the reaction liquid on to ice and filtering off as soon as possible. The anhydride is hydrolysed by hot water, the sulphuric acid removed, and the acid converted into the zinc salt. The filtrate from the precipitated zinc salt is treated with calcium chloride until no precipitate of calcium salt is obtained. The zinc salt consists of a mixture of the 3:4- and 4:5-dichlorophthalates; the calcium salt is nearly pure 3:6-salt. The 3:6-acid is the chief product of the reaction; the 3:4-acid amounts to 30—35%, and the 4:5-acid to 15—20% of the mixture.

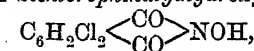
Graebe and Gourevitz's work on 3:6-dichlorophthalic acid is confirmed, and the *potassium, sodium, ammonium, calcium, barium, zinc, and silver* salts have been prepared. 3:6-Dichloroanthranilic acid, prepared from the corresponding phthalic acid, has m. p. 151—153° [Graebe and Gourevitz (*loc. cit.*) found 142°. Bamberger and Demuth, *Abstr.*, 1901, i, 392, 154.5—155° (corr.)] This acid, when heated, gives 2:5-dichloroaniline.



prepared by heating dichloroanthranilic acid and formaldehyde in methyl alcohol during one hour, crystallises in long needles, m. p. 159—161°. It

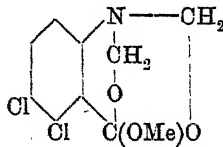
does not dissolve in alkaline carbonate, but is hydrolysed by sodium hydroxide into its components. On digestion with potassium cyanide and acidification, 3 : 6-dichlorophenylglycinenitrile-2-carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$ , is obtained; it crystallises in needles, m. p. 120—123°. The dicarboxylic acid is obtained by hydrolysing the nitrile; m. p. 159—160°.

The mixture of dichlorophthalic acids, obtained from the zinc precipitate, is converted into the anhydride, distilled, and the distillate crystallised from toluene, whereby nearly pure 4 : 5-dichloroanhydride is obtained, leaving the 3 : 4-substance in the mother liquor. To obtain the pure 3 : 4-dichlorophthalic acid, the crude 3 : 4-anhydride is first converted into the 3 : 4-dichlorophthalylhydroxylamine,

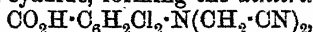


which crystallises in long needles, m. p. 218—219°. It is easily hydrolysed by dilute mineral acid to hydroxylamine and 3 : 4-dichlorophthalic acid,  $\text{C}_6\text{H}_2\text{O}_4\text{Cl}_2$ , which separates from water in small, rectangular plates, m. p. quickly heated about 195°. The alkali, calcium, barium, copper, zinc, and silver salts have been prepared. The anhydride,  $\text{C}_6\text{H}_2\text{O}_3\text{Cl}_2$ , has m. p. 120—121°, b. p. 329°.

When the dichlorophthalylhydroxylamine is heated with sodium carbonate solution, it is converted into a mixture of 5 : 6- (60—70%) and 3 : 4-dichloroanthranilic acids; these are separated by taking advantage of the zinc 3 : 4-dichloro-salt being less soluble than the 5 : 6-compound. 3 : 4-Dichloroanthranilic acid,  $\text{C}_7\text{H}_5\text{O}_2\text{NCl}_2$ , crystallises in needles, m. p. 237—238°; by heating for two hours at 240° in an atmosphere of carbon dioxide, it is partly converted into 2 : 3-dichloroaniline. By heating crude 5 : 6-dichloroanthranilic acid with formaldehyde, it is converted into a complex tricyclic compound termed by the author 5 : 6-dichloroanthranilic diformalide methyl ether (annexed formula), which crystallises in needles, m. p. 152·5°. When heated with ethyl alcohol, the ethyl ether,  $\text{C}_{11}\text{H}_{11}\text{O}_3\text{NCl}_2$ , crystallises out in needles, m. p. 123—124°. It is insoluble in alkali carbonates, but easily hydrolysed on heating. Potassium cyanide converts it into the compound,



$\text{C}_6\text{H}_2\text{Cl}_2 \begin{array}{c} \diagup \text{N}(\text{CH}_2\cdot\text{CN}) \\ \diagdown \text{CO} \end{array} \text{O} \text{CH}_2$ , of m. p. 170—173°, which yields the carboxylic acid on hydrolysis; decomp. 200°. It reacts a second time with potassium cyanide, forming the dinitrile,



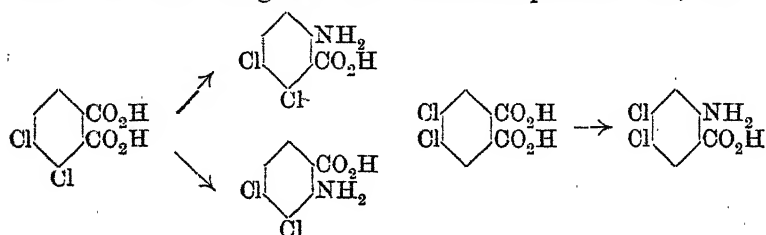
which yields the corresponding acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , decomp. 190°.

Acetaldehyde and benzaldehyde also give condensation products with this dichloroanthranilic acid, m. p. 142° (decomp.) and 179—180° respectively.

5 : 6-Dichloroanthranilic acid,  $\text{C}_7\text{H}_5\text{O}_2\text{NCl}_2$ , obtained by the hydrolysis of the formaldehyde compound, crystallises in long needles, m. p. 176—177° (decomp.), and has been characterised by preparation of metallic salts and its easy conversion into 3 : 4-dichloroaniline.

4:5-Dichlorophthalic acid,  $C_8H_4O_4Cl_2$ , crystallises in long, flat needles, m. p. on quickly heating  $200^\circ$ ; the anhydride,  $C_8H_2O_3Cl_2$ , forms prisms, m. p.  $185-187^\circ$ ; the ethyl hydrogen ester, needles, m. p.  $133-134^\circ$ ; the 4:5-dichlorophthalylhydroxylamine, m. p.  $195-197^\circ$ . The anhydride on treatment with aqueous ammonia and sodium hypochlorite yields only 4:5-dichloroanthranilic acid,  $C_7H_5O_2NCl_2$ , needles, m. p.  $213-214^\circ$ ; on heating the acid, it yields 3:4-dichloroaniline. 4:5-Dichloroanthranilic diformalide methyl ether,  $C_{10}H_9O_2NCl_2$ , forms needles, m. p.  $118-121^\circ$ ; the ethyl ether is formed by heating with ethyl alcohol, m. p.  $95-97^\circ$ , and it reacts with two molecules of potassium cyanide.

The preparation of these three dichloroanthranilic acids is a proof of the constitution assigned to the new dichlorophthalic acids, thus:



This also receives complete support by the chlorination of the two monochlorophthalic acids in fuming sulphuric acid. 3-Chlorophthalic acid gave 3:6- and 3:4-dichloro-acids; 4-chlorophthalic acid gave only 3:4- and 4:5-dichloro-acids. It is to be remarked that the monochlorophthalic acids cannot be obtained by the chlorination of the anhydride in sulphuric acid.

W. R.

[Preparation of Phenolphthalein Esters.] KNOLL & Co. (D.R.-P. 212892).—The utility of phenolphthalein diacetate when employed therapeutically has been restricted by its ready hydrolysis, whilst the dibenzoate and dibenzenesulphonate from their stability have proved useless. The employment of substituted and higher paraffin acids, or of aromatic acids, gives rise to phenolphthalein derivatives of intermediate stability and therapeutic value. *Phenolphthalein diisovalerate*, m. p.  $110^\circ$ , is a colourless, crystalline powder insoluble in, but slowly decomposed by, hot sodium hydroxide.

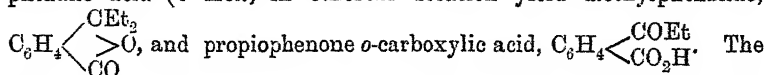
*Phenolphthalein dibutyrate* is an amorphous powder; it is decomposed by hot alkali carbonates.

*Phenolphthalein disalicylate* has m. p.  $195-198^\circ$ . *Phenolphthalein carbonate*, m. p.  $200-210^\circ$  (decomp.), is prepared by heating phenolphthalein with phenyl carbonate or with guaiacol carbonate in the presence of sodium hydroxide under diminished pressure. *Phenolphthalein dicinnamate*, m. p.  $181^\circ$ , is a crystalline powder.

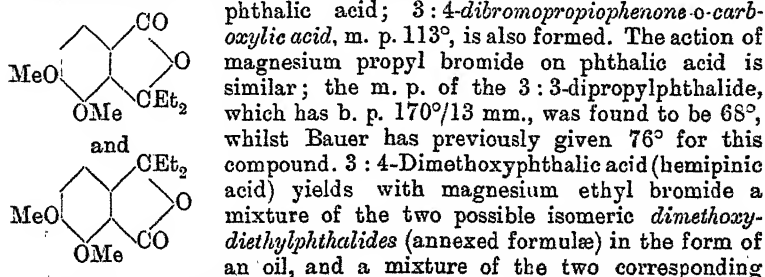
F. M. G. M.

Action of Organic Magnesium Compounds on Dicarboxylic Acids and a Method of Converting a  $\cdot CO_2H$  Group into  $\cdot CO\cdot R$ . HUGO SIMONIS and K. ARAND (*Ber.*, 1909, 42, 3721-3728).—The

interaction of magnesium alkyl halides and phthalic acid leads to the formation of both ketonic and tertiary alcoholic derivatives. In the former the  $\cdot\text{CO}_2\text{H}$  group has been converted into  $\cdot\text{COR}$  by the following series of changes:  $\cdot\text{CO}_2\text{H} \rightarrow \cdot\text{CO}_2\text{Mg}\cdot\text{X} \rightarrow \cdot\text{C}(\text{OMgX})_2\cdot\text{R} \rightarrow \cdot\text{C}(\text{OH})_2\cdot\text{R} \rightarrow \cdot\text{CO}\cdot\text{R}$ . Magnesium ethyl bromide (8 mols.) and phthalic acid (1 mol.) in ethereal solution yield diethylphthalide,



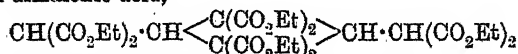
latter has at first the m. p.,  $91^\circ$ , previously given by Gabriel and Michael, but this rises on recrystallisation to  $97^\circ$ . 5:6-Dibromo-3:3-diethylphthalide, m. p.  $103^\circ$ , is similarly obtained from 4:5-dibromophthalic acid; 3:4-dibromopropiophenone-*o*-carb-



oxydiethylphthalides (annexed formulæ) in the form of an oil, and a mixture of the two corresponding dimethoxypropiophenone-*o*-carboxylic acids, which were also not separated, although selected crystals had different m. p. ( $85^\circ$  and  $113^\circ$  respectively).

R. V. S.

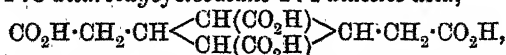
*cyclo*Butane Derivatives as Products of the Polymerisation of Ethyl Dicarboxylglutaconate. MAX GUTHZEIT, ARNO WEISS, and WALTER SCHAEFER (*J. pr. Chem.*, 1909, [ii], 80, 393—449).—The nature of the isomerism of the two bimolecular esters, m. p.  $103^\circ$  and  $88^\circ$ , derived from ethyl dicarboxylglutaconate still remains unsolved, but further evidence has been obtained which supports the view that the ester, m. p.  $103^\circ$ , is the ethyl ester of 1:1:3:3-tetracarboxycyclobutane-2:4-dimalonic acid,



(compare Guthzeit and Weiss, *Abstr.*, 1901, i, 314).

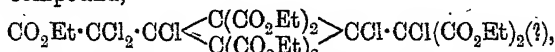
Four isomeric tetracarboxylic acids,  $\text{C}_{10}\text{H}_{12}\text{O}_8$ , have been obtained during the investigation, namely, two from the ester, m. p.  $103^\circ$ , a third from the isomeric ester, m. p.  $88^\circ$ , and a fourth from the bimolecular ester derived from ethyl isoaconitate (*loc. cit.*); they are isomeric 1:3-dicarboxycyclobutane-2:4-diacetic acids, but the nature of the isomerism is not known.

Ethyl 1:1:3:3-tetracarboxycyclobutane-2:4-dimalonic acid, m. p.  $103^\circ$ , when boiled with concentrated hydrochloric acid yields a mixture of 1:3-dicarboxycyclobutane-2:4-diacetic acid,

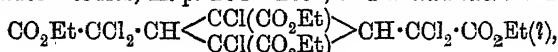


m. p.  $127^\circ$ — $128^\circ$ , the methyl ester of which,  $\text{C}_{14}\text{H}_{20}\text{O}_8$ , is an oil, and 1:3-dicarboxycyclobutane-2:4-diacetic acid, m. p.  $234^\circ$ , the methyl ester

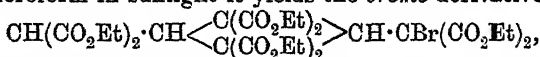
of which forms long, compact prisms, m. p. 76—77°. The ester, m. p. 103°, undergoes the following changes: (1) It is converted by aniline at 140—150° into malonanilide and ethyl  $\beta$ -anilinoethylene- $\alpha$ -dicarboxylate, and by a concentrated alcoholic solution of ammonia into malonamide and ethyl aminoethylenedicarboxylate; (2) when treated with ethyl iodide and zinc, it yields ethyl diethylcarboxyglutaconate and ethyl diethylmalonate, the latter being a decomposition product of the former; (3) it is converted by chlorine at 130—150° into a *pentachloro*-compound,



small, slender needles, m. p. 204—205°, and a *hexachloro*-compound,



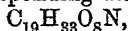
small prisms, m. p. 178—180°; (4) when acted on by bromine in boiling chloroform in sunlight it yields the *bromo*-derivative,



which crystallises in large, compact prisms, m. p. 78—80°, and the analogous *dibromo*-derivative,  $\text{C}_{30}\text{H}_{42}\text{O}_{16}\text{Br}_2$ , colourless prisms, m. p. 147—148°. A *pentabromo*-compound,  $\text{C}_6\text{Br}_5(\text{CO}_2\text{Et})_7$ , crystallising in prisms, m. p. 215—217°, is formed when bromine is added to a hot solution of the ester in glacial acetic acid.

The *cyclobutane* ester, m. p. 88°, when boiled with concentrated hydrochloric acid yields a *dicarboxycyclobutanediacetic acid*,  $\text{C}_{10}\text{H}_{12}\text{O}_8$ , m. p. 184°.

The interaction of equivalent quantities of ethyl dicarboxyglutaconate and piperidine results in the formation of the *piperidinium* salt,  $\text{C}(\text{CO}_2\text{Et})_2 \cdot \text{CH} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{OEt}) \cdot \text{O} \cdot \text{C}_5\text{NH}_{12}$ , which crystallises in yellow needles, m. p. 94°, and is probably an intermediate product in the transformation of ethyl dicarboxyglutaconate into the bimolecular ester, m. p. 103°. The corresponding *diethylammonium* salt,



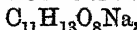
forms yellow needles, m. p. 131—132°; ethyl dicarboxyglutaconate does not polymerise under the influence of diethylamine. The *mercuric* salt,  $\text{C}_{30}\text{H}_{42}\text{O}_{16}\text{Hg}$ , is a yellowish-green, viscid oil. The complex *mercury* compound,  $\text{C}_{15}\text{H}_{20}\text{O}_8\text{Hg}(\text{OH})_3 \cdot 3\text{Hg} \cdot \text{OAc} (?)$ , crystallising in small, slender, white needles, is formed by the action of mercuric acetate on the sodium derivative of the ester.

The bimolecular ester derived from ethyl *isoaconitate*, in analogy to the esters obtained from ethyl dicarboxyglutaconate, must have the formula  $\text{CH}(\text{CO}_2\text{Et})_2 \cdot \text{CH} \left\langle \begin{array}{c} \text{CH}(\text{CO}_2\text{Et}) \\ \text{CH}(\text{CO}_2\text{Et}) \end{array} \right\rangle \text{CH} \cdot \text{CH}(\text{CO}_2\text{Et})_2$ ; when boiled with 10% hydrochloric acid it yields a *dicarboxycyclobutanediacetic acid*,  $\text{C}_{10}\text{H}_{12}\text{O}_8$ , identical with von Pechmann's bimolecular glutaconic acid (compare Abstr., 1899, i, 870).

*Methyl dicarboxyglutaconate*,

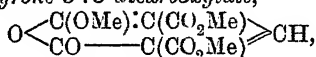


a colourless viscid oil, is obtained as the *sodium* derivative,



m. p. 247—248°, by the interaction of methyl malonate and chloro-

form in the presence of sodium methoxide; the analogous *copper* derivative,  $(C_{11}H_{13}O_8)_2Cu$ , forms microscopic prisms, m. p. 245—246°; the *mercuric* derivative,  $(C_{11}H_{13}O_8)_2Hg$ , crystallises in prisms, m. p. 156°; the *mercuriacetate*,  $C_{11}H_{13}O_7 \cdot O \cdot Hg \cdot OAc$ , crystallising in stellate groups of small needles, m. p. 147—148°, is obtained when an excess of mercuric acetate is used in the preparation of the normal mercuric salt; the *mercurichloride*,  $C_{11}H_{13}O_7 \cdot OHgCl$ , forms tufts of prisms, m. p. 178—180°. The parent substance when treated with an ethereal solution of piperidine yields the *methyl* ester of 1:1:3:3-tetracarboxy-*cyclobutane-2:4-dimalonic acid*,  $C_{23}H_{23}O_{16}$ , glistening prisms, m. p. 221—222°, and when heated at 220° under a pre-sure of 20 mm. yields *methyl 6-methoxy-2-pyrone-3:5-dicarboxylate*,



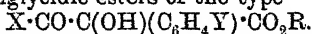
very small prisms, m. p. 128—129°.

The action of chlorine on ethyl ethane- $\alpha\alpha\beta\beta$ -tetracarboxylate and ethyl cyclobutane-1:1:3:3-tetracarboxylate was investigated for purposes of comparison; the latter compound yields a *tetrachloro*-derivative,  $(\text{CO}_2\text{Et})_2\text{C} \begin{smallmatrix} \diagup \text{CCl}_2 \\ \diagdown \text{CCl}_2 \end{smallmatrix} \text{C}(\text{CO}_2\text{Et})_2$ , obtained as a viscid syrup; the first named yields a chlorinated product with elimination of an ethylcarboxy-group.

W. H. G.

**Identity of Helianthic Acid and Chlorogenic Acid.** K. GORTER (*Arch. Pharm.*, 1909, 247, 436-438).—The properties ascribed by Ludwig and Kromeyer to helianthic acid, isolated from sunflower seeds, show the greatest similarity to those of chlorogenic acid (this vol., i, 588). The author therefore has isolated helianthic acid in a crystalline form, and proved its identity with chlorogenic acid by a comparison of the m. p.'s, specific rotations, calcium salts, and acetyl derivatives. C. S.

**New General Methods for the Synthesis of Aromatic Aldehydes.** ALFRED GUYOT (*Compt. rend.*, 1909, 149, 789—790).—The  $\alpha\beta$ -diketonic esters (Bouveault, *Abstr.*, 1904, i, 556; 1907, i, 217) combine with aromatic hydrocarbons, phenols, and tertiary amines, forming acylphenylglycidic esters of the type



Condensation occurs in the para-position to the substituent, or where this is already occupied, in the ortho-position. Zinc chloride is employed to effect condensation in the case of the phenols, and sulphuric acid in the case of amines. In the latter instance the product is accompanied by compounds of the type  $X \cdot CO \cdot C(C_6H_4Y)_2 \cdot CO_2R$ , arising from further condensation.

The acetylphenylglycollic esters prepared in this way undergo quantitative decomposition when treated by any of the following methods: (1) On warming with excess of concentrated sulphuric acid, when the following reaction occurs:  $X \cdot CO \cdot C(OH)(C_6H_4Y) \cdot CO_2R + 2H_2O = Y \cdot C_6H_4 \cdot CH(OH) \cdot CO_2H + X \cdot CO_2H + R \cdot OH$ . The hydroxy-acid then loses water and carbon monoxide, and gives the aldehyde,  $Y \cdot C_6H_4 \cdot CHO$ . (2) On boiling with an aqueous solution of a copper

salt, when oxidation occurs with formation of a phenylglyoxylic acid; this loses carbon dioxide when boiled with dimethyl-*p*-toluidine, forming the aldehyde. (3) On hydrolysis with aqueous potassium hydroxide, the corresponding phenylglycollic acid is formed; this need not be isolated, since the aldehyde is readily obtained by oxidising the solution with potassium ferricyanide.

The  $\alpha\beta$ -diketonic esters used in the foregoing syntheses can be replaced by mesoxalic esters (compare this vol., i, 159, 236, 306).

W. O. W.

**Benzaldehydesulphoxylate and Acetonesulphoxylate.** EMIL FROMM and F. ERFURT (*Ber.*, 1909, 42, 3812—3816).—Formaldehyde reacts with sodium hyposulphite to form formaldehydesulphoxylate (rongalite). According to Bazlen (*Abstr.*, 1905, ii, 240), sodium benzaldehydesulphoxylate,  $\text{NaSO}_3\text{C}_7\text{H}_7$ , is formed by the action of benzaldehyde and sodium hyposulphite in presence of sodium hydroxide. This product is now shown to be benzaldehyde bisulphite; in addition, the hyposulphite is in part oxidised to sulphite and in part reduced to disulphite. Acetone acts similarly to benzaldehyde; formaldehyde is the only compound which forms sulphoxylate.

E. F. A.

**Action of Sodium Disulphide on Ring-Substituted *p*-Nitrotoluenes.** JAN. J. BLANKSMA (*Chem. Weekblad*, 1909, 6, 899—913).—Ring-substituted *p*-nitrotoluenes are converted by an alcoholic solution of sodium disulphide into the corresponding ring-substituted *p*-aminobenzaldehydes and *p*-toluidines, the latter being volatile with steam. The amino-groups in the resulting aldehydes are replaceable by halogen atoms or other groups, thus affording a means of preparing substitution products of benzaldehyde.

Bromine water converts *p*-aminobenzaldehyde into 3:5-dibromo-4-aminobenzaldehyde, which forms colourless crystals, m. p. 150°. 2-Chloro-4-aminobenzaldehyde changes in a few hours to an infusible *modification*, insoluble in water, alcohol, or ether. Both forms are converted by acetic anhydride into 2-chloro-4-acetylaminobenzaldehyde, m. p. 152°, which is transformed by acetic anhydride and a small proportion of concentrated sulphuric acid into 2-chloro-4-acetylaminobenzylidene diacetate,  $\text{NHAc}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CH}(\text{OAc})_2$ , m. p. 132°. Warming with alcoholic hydrochloric acid decomposes this substance into 2-chloro-4-aminobenzaldehyde and acetic acid. 2-Chloro-4-acetylaminobenzoic acid, which forms colourless crystals, m. p. 206°, is obtained by oxidising 2-chloro-4-acetylaminobenzaldehyde or 2-chloro-aceto-*p*-toluidide with potassium permanganate. Boiling with hydrochloric acid converts it into 2-chloro-4-aminobenzoic acid, whilst bromine water precipitates 3-chloro-2:4:6-tribromonaniline.

2-Chloro-*p*-toluidine is separated by steam distillation from the products of the interaction of sodium disulphide and 2-chloro-4-nitrotoluene. With acetic anhydride it yields 2-chloroaceto-*p*-toluidide, m. p. 104°. Wynne and Greeves (*Proc.*, 1895, 11, 151) give 86°, but their compound contained  $1\text{H}_2\text{O}$ . Glacial acetic acid and acetic anhydride

convert 2-bromo-4-aminobenzaldehyde into 2-bromo-4-acetylamino-benzaldehyde, crystallising in pale yellow needles, m. p. 135°. 2-Bromo-*p*-toluidine and acetic anhydride yield 2-bromoaceto-*p*-toluidide, which forms colourless crystals, m. p. 113°. Boiling with potassium permanganate in aqueous solution converts the last compound into 2-bromo-4-acetylamino-benzoic acid, colourless crystals, m. p. 206°, which on boiling with hydrochloric acid yields 2-bromo-4-amino-benzoic acid, crystallising in colourless needles, m. p. 202° (decomp.). Bromine water converts this acid into 2 : 3 : 4 : 6-tetrabromoaniline.

2-Iodo-4-nitrotoluene is converted by sodium disulphide into 2-iodo-*p*-toluidine, volatile with steam. It forms colourless crystals, m. p. 38°, and with acetic anhydride yields 2-iodoaceto-*p*-toluidide (Willgerodt and Gartner, Abstr., 1908, i, 876). The residue from the steam distillation of 2-iodo-*p*-toluidine contains 2-iodo-4-amino-benzaldehyde, which crystallises in yellow needles, m. p. 136°. It changes more rapidly than the corresponding chloro- and bromo-derivatives to an infusible, insoluble modification, which is converted by glacial acetic acid and acetic anhydride into 2-iodo-4-acetylamino-benzaldehyde, yellow crystals, m. p. 144°.

By the Sandmeyer reaction, *p*-aminobenzaldehyde yields *p*-chlorobenzaldehyde (von Walther and Raetze, Abstr., 1902, i, 466), *p*-bromobenzaldehyde (Jackson and White, Abstr., 1878, 728), and *p*-iodobenzaldehyde (Hantzsch, Abstr., 1894, i, 331). The same reaction converts 2-chloro-4-aminobenzaldehyde into 2 : 4-dichlorobenzaldehyde (Erdmann and Schwechten, Abstr., 1891, 448), and 2-bromo-4-aminobenzaldehyde into 2 : 4-dibromobenzaldehyde, colourless crystals, m. p. 80°, which is oxidised by potassium permanganate to 2 : 4-dibromobenzoic acid.

3 : 5-Dibromobenzaldehyde is obtained by diazotisation of 3 : 5-dibromo-4-aminobenzaldehyde, and is volatile with steam. It forms colourless crystals, m. p. 90°, and is oxidised by permanganate to 3 : 5-dibromobenzoic acid.

2 : 4-Diiodobenzaldehyde is obtained by treating diazotised 2-iodo-4-aminobenzaldehyde (soluble form) with potassium iodide. It forms colourless crystals, m. p. 129°, which quickly become pale yellow.

A. J. W.

**Bromine Derivatives of *o*-Amino- and of *o*-Hydroxy-benzaldehyde.** JULIUS MÜLLER (*Ber.*, 1909, 42, 3695—3703).—5-Bromosalicylaldehyde has been the only known monobrominated salicylaldehyde. The author now describes isomerides containing the bromine in positions 3 and 4, and incidentally mentions other new compounds.

4-Bromosalicylaldehyde, m. p. 52°, is produced by reducing 4-bromo-2-nitrobenzaldehyde by ferrous sulphate and ammonium hydroxide to 4-bromo-2-aminobenzaldehyde, m. p. 85°, which is dissolved in 50% acetic acid and diazotised by sodium nitrite and sulphuric acid, the solution being subsequently heated to 90°. It has a pleasant, aromatic odour, gives a reddish-violet coloration with ferric chloride, dissolves in sodium hydroxide, and forms a sodium hydrogen sulphite compound,

*phenylhydrazone*, m. p. 145°, *oxime*, m. p. 151°, and an *acetyl* derivative, m. p. 92°.

4-Bromo-2-aminobenzaldoxime, m. p. 194°, is obtained by the interaction of the corresponding aldehyde, hydroxylamine hydrochloride, and anhydrous sodium carbonate in the presence of alcohol, or by reducing an alcoholic solution of 4-bromo-2-nitrobenzaldoxime by ammonium sulphide. 4-Bromo-2-aminobenzaldehydephenylhydrazone has m. p. 215°.

3-Bromosalicylaldehyde, m. p. 49°, is obtained by adding finely-powdered 3-nitrosalicylaldehyde to a cold solution of stannous chloride in hydrochloric acid, isolating the yellow stannichloride obtained by warming, and suspending it in dilute hydrochloric acid; the suspension is diazotised and added to a hot solution of cuprous bromide. The aldehyde is volatile with steam, soluble in sodium hydroxide or carbonate, and forms an *oxime*, m. p. 165°; *phenylhydrazone*, m. p. 100°; and *semicarbazone*, m. p. 266°.

3-Bromo-2-acetoxybenzonitrile, m. p. 49—50°, obtained by heating 3-bromosalicylaldoxime, anhydrous sodium acetate, and acetic anhydride at 160—170° for four hours, is rapidly hydrolysed by cold concentrated sulphuric acid, yielding 3-bromosalicylamide, m. p. 165°, which is converted by boiling moderately concentrated hydrochloric acid into 3-bromosalicylic acid, m. p. 184°, identical with Lellmann and Grothmann's compound. C. S.

Condensation of Aldehydes and Hydroxyaldehydes with Phenols. P. DANCKWORTT (*Ber.*, 1909, 42, 4163—4171).—With the object of ascertaining the molecular proportions in which aldehydes condense with phenols in the presence of hydrochloric acid, *p*-nitrobenzaldehyde, nitrovanillin, the monobrominated *o*-, *m*-, and *p*-hydroxybenzaldehydes, bromopiperonal, and bromocinnamaldehyde have been submitted to the following process. The aldehyde (1 mol.) and a phenol (2 mols.) are dissolved in glacial acetic acid and treated with concentrated hydrochloric acid. Sooner or later a precipitate is formed in the cold, which is collected, washed with water, and finally with ether, benzene, or chloroform to remove unchanged material. The products are amorphous, and usually exhibit haloechromy. In the cold, bromovanillin unites with phenol itself in the proportion 1 : 2, and with polyhydric phenols in equal molecular proportions, a second molecule of the phenol being added after long warming. *p*-Nitrobenzaldehyde combines always with 2 mols. of a phenol. 5-Bromosalicylaldehyde combines with 1 mol. of resorcinol, the isomeric *m*- and *p*-compounds with 2 mols. Bromopiperonal condenses with 1 mol. of resorcinol, and bromocinnamaldehyde with 2 mols. C. S.

Phenyl Vinyl Ketone and some of its Homologues. ELMER P. KOHLER (*Amer. Chem. J.*, 1909, 42, 375—401).—By the action of acrylyl chloride on benzene in presence of aluminium chloride, Moureu (*Abstr.*, 1894, i, 30) obtained a small quantity of a colourless substance which he regarded as phenyl vinyl ketone. Klages (*Chem. Zeit.*, 1908, 33, 318), however, did not accept this conclusion, and stated that phenyl vinyl ketone and its homologues can be obtained

by the action of alcoholic potassium hydroxide on  $\alpha$ -bromo-ketones. It has already been shown (this vol., i, 394) that Klages' products are mixtures which do not contain any unsaturated ketone.

The author has now repeated Moureu's work, and finds that his supposed phenyl vinyl ketone is  $\alpha$ -hydrindone. This is doubtless formed from phenyl vinyl ketone, since the latter is readily converted into  $\alpha$ -hydrindone by the action of aluminium chloride. It has been found that phenyl vinyl ketone can be obtained by the action of potassium iodide on  $\alpha\beta$ -dibromopropiophenone, but the product of this reaction always contains  $\beta$ -ethoxypropiophenone, owing to the fact that in presence of minute quantities of acid, phenyl vinyl ketone is capable of uniting with the alcohol employed as a solvent. This method has been extended to the preparation of phenyl propenyl ketone and phenyl isobutenyl ketone.

An improved method is described for the preparation of  $\alpha\beta$ -dibromopropionic acid.  $\alpha\beta$ -Dibromopropionyl chloride reacts with benzene in presence of aluminium chloride to form  $\alpha\beta$ -dibromopropiophenone,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{COPh}$ , m. p.  $58^\circ$ , which crystallises in large needles or plates, and on reduction with zinc dust is converted into a mixture of propiophenone and dibenzoylbutane; the latter substance melts at  $112^\circ$ , and its oxime at  $232^\circ$  (compare Etaix, Abstr., 1898, i, 125).

*Phenyl vinyl ketone*,  $\text{CH}_2\text{:CH}\cdot\text{COPh}$ , b. p.  $115^\circ/18$  mm., is very reactive; it instantaneously reduces potassium permanganate, combines energetically with bromine, hydrogen halides, and primary and secondary amines, and polymerises when exposed to sunlight or when gently heated. The ketone reacts readily with phenylhydrazine with formation of 1 : 3-diphenylpyrazoline,  $\text{CPh}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{Ph} \end{smallmatrix}$  (or possibly the

1 : 5-compound), m. p.  $158^\circ$ , which forms large, yellow needles. *Ethoxypropiophenone*,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COPh}$ , m. p. about  $12^\circ$ , b. p.  $135^\circ/18$  mm., yields a *phenylhydrazone*, m. p.  $86^\circ$ .  $\beta$ -Chloropropiophenone,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COPh}$ , m. p.  $57^\circ$ , obtained by the combination of phenyl vinyl ketone with hydrogen chloride, crystallises in large plates. Phenyl vinyl ketone unites readily with sodium hydrogen sulphite with formation of *sodium benzoylethanesulphonate*, which separates in large, colourless plates containing  $1\text{H}_2\text{O}$ .  $\beta$ -Benzoylethanesulphonic acid,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ , m. p.  $95^\circ$ , forms colourless needles. By the action of magnesium methyl iodide on phenyl vinyl ketone, phenyl propyl ketone is obtained, and by the action of magnesium phenyl bromide,  $\beta$ -phenylpropiophenone is produced. 4-Bromophenyl  $\alpha\beta$ -dibromoethyl ketone,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br}$ , m. p.  $74^\circ$ , prepared from bromopropionyl chloride and bromobenzene by Friedel and Crafts' reaction, forms large prisms, and by the action of potassium iodide is converted into 4-bromophenyl  $\beta$ -ethoxyethyl ketone,

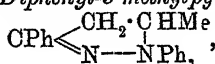
$\text{OEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br}$ , m. p.  $54^\circ$ , which crystallises in large, colourless plates, and yields a *phenylhydrazone*, m. p.  $108^\circ$ .

$\alpha\beta$ -Dibromobutyryl chloride,  $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{COCl}$ , b. p.  $112^\circ/20$  mm., prepared from the dibromobutyric acid obtained by treating crotonic acid with bromine, reacts with benzene in presence of aluminium chloride to form  $\alpha\beta$ -dibromobutyrophenone  $\text{CHMeBr}\cdot\text{CHBr}\cdot\text{COPh}$ ,

m. p. 112°, which crystallises in needles. The latter compound is converted by potassium iodide into *phenyl propenyl ketone*,



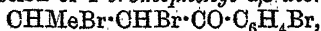
b. p. 135°/20 mm., which can also be prepared by treating *crotonyl chloride*,  $\text{CHMe}:\text{CH}:\text{COCl}$ , b. p. 126°, with benzene in presence of aluminium chloride. 1:3-*Diphenyl-5-methylpyrazoline*,



m. p. 108°, obtained by the action of phenylhydrazine on phenyl propenyl ketone, forms thin, yellow plates. The ketone reacts with magnesium methyl iodide to form *isovalerophenone*, and with magnesium phenyl bromide to form  $\beta$ -phenylbutyrophenone.

*Bromophenyl propenyl ketone*,  $\text{CHMe}:\text{CH}:\text{CO} \cdot \text{C}_6\text{H}_4\text{Br}$ , m. p. 47°, reacts with phenylhydrazine to form 1-phenyl-5-bromophenyl-3-methylpyrazoline,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{C} \begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{NPh} \end{array}$ , m. p. 136°, and unites with

bromine with production of 4-bromophenyl  $\alpha\beta$ -dibromopropyl ketone,



m. p. 76°, which crystallises in needles.

*Dibromoisovaleryl chloride*,  $\text{CMe}_2\text{Br} \cdot \text{CHBr} \cdot \text{COCl}$ , b. p. 126—130°/20 mm., prepared from the dibromo-acid obtained by treating  $\beta\beta$ -dimethylacrylic acid with bromine, is converted by Friedel and Crafts' reaction into *dibromoisovalerophenone*,  $\text{CMe}_2\text{Br} \cdot \text{CHBr} \cdot \text{COPh}$ , m. p. 81°, which crystallises in needles. This dibromo-ketone is converted by potassium iodide into *phenyl isobutenyl ketone*,  $\text{CMe}_2:\text{CH}:\text{COPh}$ , b. p. 148°/22 mm., a colourless liquid, which yields a *phenylhydrazone*, m. p. 88°, and reacts with magnesium phenyl bromide with formation of  $\beta$ -phenylisobutyrophenone and an unsaturated compound, and, on oxidation with potassium permanganate, is converted into benzo-phenone.  $\beta$ -Phenylisobutyrophenone yields a *phenylhydrazone*, m. p. 94°, and two *oximes*, m. p. 85° and 111°, which crystallise in needles and plates respectively.

E. G.

[Condensation Products of Amino- and Chloro-anthraquinones.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212470).—By the condensation of substituted 1-aminoanthraquinones with substituted 2-chloroanthraquinones at high temperatures or under pressure, substituted  $\alpha\beta$ -dianthraquinoneimides are obtained. Condensation products from the following compounds are mentioned in the patent. 6-Chloro-1-methylaminoanthraquinone, prepared from 6-chloro-1-nitroanthraquinone and methylamine; 7-chloro-1-methylaminoanthraquinone; 1-amino-6- and 1-amino-7-methylaminoanthraquinone from 6(7)-chloro-1-aminoanthraquinone and methylamine; 2-chloroanthraquinone; 2-chloro-5- and 2-chloro-8-methylaminoanthraquinones; 2-chloro-5- and 2-chloro-8-aminotolylanthraquinones, obtained from 2-chloro-5- and 2-chloro-8-nitroanthraquinone and *p*-toluidine; 2-chloro-5- and 2-chloro-8-methoxyanthraquinones, obtained from 2-chloro-5- or 2-chloro-8-nitroanthraquinone; 2-chloro-5- and -8-oxyanthraquinones, prepared from sodium 5-nitro-2-anthraquinonesulphonate; 2-chloro-8-acetylaminoanthraquinone, prepared from 2-chloro-8-aminoanthraquinone. The

product obtained by fusing 6(or 7)-chloro-1-acetylaminoanthraquinone with phosphoryl chloride. 5- or 8-Aminoanthraquinone-2:3-quinoline, obtained by the nitration and subsequent reduction of anthraquinonyl-2:3-quinoline; 5- or 8-aminoanthraquinonyl-2:1-quinolines, obtained in the same way from anthraquinonyl-2:1-quinoline; 5- or 8-amino-2:3-anthraquinoline; 2-chloro-5-acetylaminoanthraquinoline.

F. M. G. M.

**Preparation of Xanthopurpurin.** FARBERWERKE VORM MEISTER, LUCIUS & BRÜNING (D.R.-P. 212697).—A quantitative yield of 1:3-dihydroxyanthraquinone (xanthopurpurin) is obtained when a 20% aqueous suspension of purpurin mixed with ammonium hydroxide is treated at the ordinary temperature with sodium hyposulphite until the red colour disappears.

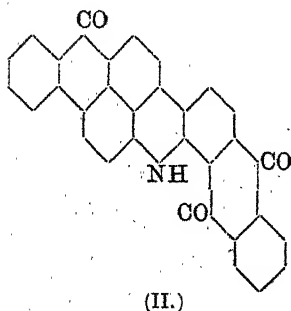
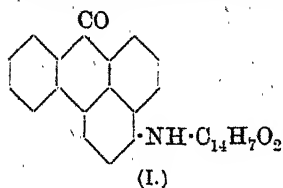
F. M. G. M.

**Preparation of Dithioanthraquinones.** FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P. 212857).—Sodium thiolanthraquinone disulphide (this vol., i, 496) can be prepared by boiling an alcoholic solution of potassium anthraquinone- $\alpha$ -sulphonate with sodium hydrosulphide.

*Sodium 1:5-dithiolanthraquinone*, dark brown needles, is prepared by boiling sodium anthraquinone-1:5-disulphonate with sodium sulphide in aqueous solution.

F. M. G. M.

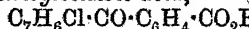
[Preparation of Benzanthranyl-1-aminoanthraquinone Derivatives.]



BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212471).—The condensation of 1-aminoanthraquinone with halogenated benzantrones at high temperatures leads to the formation of 1-benzanthranyl-1-aminoanthraquinones (formula I). These on further condensation lose two atoms of hydrogen and yield compounds (formula II) which on treatment with alkaline hyposulphite produce vat dyes.

F. M. G. M.

[Preparation of Substituted  $\omega$ -Halogenmethylantraquinones.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 211967).—*o*-Chloromethylbenzoylbenzoic acid,



m. p. 173°, is prepared by adding aluminium chloride to a warm solution

of phthalic anhydride in *o*-chlorotoluene and heating at 70° during half an hour. By heating the foregoing acid at 110—135° with sulphuric acid, two isomeric chloromethylantraquinones are formed. These form yellow needles, m. p. 215° and 165° respectively.

*Bromomethylantraquinone* is obtained in an analogous manner from

*o*-bromotoluene. *Dichloromethylantracquinone*, m. p. 205°, is prepared by chlorinating chloromethylantracquinone at 210–220°. These compounds, when fused with sulphur, are used for the preparation of dyes.  
F. M. G. M.

**History of the Terpenes.** IWAN KONDAKOFF (*J. pr. Chem.*, 1909, [ii], 80, 455–468).—Polemical. A criticism of Wallach's work, *Terpene und Campher*.  
W. H. G.

*l*-Pinene and its Isomeric Change into Dipentene. WLADIMIR A. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 996–1004. Compare Abstr., 1908, i, 278).—According to Flawitzky's investigations (Abstr., 1887, 968), the action of sulphuric acid on *l*-pinene results first in the rupture of the 4-carbon atom ring with formation of optically active terpene hydrate (terpineol), the latter then undergoing dehydration to *l*-isoterpene (limonene), which is subsequently converted into dipentene.

The author has followed polarimetrically the action of alcoholic sulphuric acid and water (1 mol.) on *l*-pinene (1 mol.). The rotation of the mixture at first increases to a maximum, and then gradually diminishes. Fractionation of the products at a stage where the rotation had not quite reached the maximum value revealed the presence of an ether,  $C_{10}H_{17}\cdot OEt$ , b. p. 216–217°/740 mm.,  $D_4^{25}$  0.9010,  $n_D^{25}$  1.4649,  $[\alpha]_D - 66.95^\circ$ . Later, when the rotation had reached its maximum value, the products were found to contain, in addition to this ether, the corresponding alcohol,  $C_{10}H_{17}\cdot OH$ , formed by hydrolysis of the ether.

Fractionation of *l*-pinene always yields a large part boiling considerably below 155°, the b. p. of *l*-pinene. The conclusion is drawn that *l*-pinene is not a chemical individual, but consists of a mixture of hydrocarbons, possibly of pinene and fenchene. This conclusion is also indicated by the results of Bouchardat and Lafont (Abstr., 1894, i, 612; 1898, i, 442; 1899, i, 156) and of Barbier and Grignard (Abstr., 1908, i, 94, 852), who found that, in the hydration of *l*-pinene, fenchyl alcohol and borneol are formed in addition to the normal product, terpeneol. The author has confirmed these results, and has also demonstrated the presence of fenchene in *l*-pinene, which probably contains camphene as well.  
T. H. P.

**Constituents of Ethereal Oils.** Carvenene,  $C_{10}H_{16}$ , and "Terpinene." FRIEDRICH W. SEMMLER (*Ber.*, 1909, 42, 4171–4174. Compare this vol., i, 110; Wallach, *ibid.*, i, 726; Auwers, *ibid.*, i, 592, 596).—The  $\alpha$ -terpinene, obtained by Auwers from *o*-cresol, does not agree with other terpinenes in its physical data; probably intramolecular change occurs during one or other of the many reactions by which it is produced. Wallach's statement, that a relatively pure chloro-terpinene (chlorocarvenene) can only be obtained with the greatest difficulty by the action of phosphorus pentachloride on carvenone, is refuted, since the author finds that a very smooth reaction occurs when the two substances are shaken for about one hour in light petroleum. Carvenene prepared by the author's process is free from cymene, and is oxidised by cold alkaline potassium permanganate to

$\alpha$ , $\delta$ -dihydroxy- $\alpha$ -methyl- $\delta$ -isopropyladipic acid, m. p. 189°. Carvenene is therefore  $\Delta^{1,3}$ -dihydrocymene (Wallach's  $\alpha$ -terpinene), and is claimed by the author to be the purest sample hitherto obtained. C. S.

**Terpenes of Rosin Spirit.** CARLO GRIMALDI (*Chem. Zeit.*, 1909, 33, 1157).—The only terpenes previously recorded as present in "rosin spirit" are pinene and dipentene. The author confirms the presence of both these substances, and in addition has found camphene in "spirits" prepared from American and Austrian rosins. No phellandrene, sylvestrene, or limonene was found. T. A. H.

***l*-Camphene.** P. G. GOLUBEFF (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1004—1014).—The author has succeeded in isolating from the ethereal oil of the Siberian fir, pure natural *l*-camphene, m. p. 50°, b. p. 159—160°,  $[\alpha]_D -92.37^\circ$  (compare Abstr., 1905, i, 74), in the form of opaque, volatile crystals, which gradually become transparent.

The action of a mixture of acetic acid and 50% sulphuric acid, in the proportions employed by Bertram and Walbaum (Abstr., 1894, i, 204), on this pure camphene yields, after three hours at 50—60°, 75.1% of isoborneol acetate,  $C_{10}H_{17}OAc$ ; after six hours at 50—60°, 75.81%; after nine hours at 50—60°, 81.3%, and after two hours at 70—80°, 79.45% of the acetate. After heating at 50—60°, the hydrolysed products are slightly dextrorotatory, whilst at 70—80° they become inactive. The isoborneol obtained from the acetate is optically inactive, and has the same crystalline form as the isoborneol prepared from artificial camphene. On oxidation with permanganate, this isoborneol gives a camphor identical with that obtained by Bertram and Walbaum (*loc. cit.*) by oxidising the isoborneol yielded by artificial camphene and exhibiting all the ordinary characters of Japan camphor, from which it differs only in being optically inactive.

Beside the principal product, isoborneol, of the action of sulphuric and acetic acids on *l*-camphene, there are formed also *i*-camphene, identical in its chemical properties with *l*-camphene, and, probably, cymene. T. H. P.

**Carrot Oil, the Ethereal Oil of the Fruit of *Daucus Carota*.** ERWIN RICHTER (*Arch. Pharm.*, 1909, 247, 391—413).—The ethereal oil is a pale golden-yellow liquid with a characteristic, not unpleasant odour, and has  $D_{15} 0.9439$  and  $[\alpha]_D^{15} -13.38^\circ$ . It does not contain sulphur, nitrogen, or methoxyl groups. The acid number is 2.04, ester number 18.22, saponification number 20.26; after acetylation the saponification and ester numbers are 95.5 and 69.97 respectively. It contains 0.04% of isobutyric acid and 0.8% of palmitic acid. The presence of aldehydes cannot be established with certainty. After being treated with sodium carbonate, potassium hydroxide, and sodium hydrogen sulphite, the oil is hydrolysed by 5% alcoholic potassium hydroxide; the volatile acids thereby obtained are acetic and probably formic acids. The oil, after hydrolysis, is dried and fractionally distilled. Fractions I and II, b. p. 150—160° and 160—170°

respectively, contained terpenes, but these could not be isolated. A fresh portion of the oil, therefore, was distilled with alcohol, whereby the terpenes were removed, whilst the higher-boiling sesquiterpenes and oxygenated substances remained in the distilling vessel. The mixture of terpenes thus obtained was proved to contain  $\alpha$ -pinene and *l*-limonene.

The higher-boiling fractions, b. p. 100—125°/18 mm., 125—155°/18 mm., 155—160°/18 mm., and 160—180°/18 mm., solidify more or less completely by cooling, and contain an alcohol, which is isolated by the xanthogenic method.

The alcohol, *daucol*,  $C_{15}H_{25}O_2$ , m. p. 115—116°, is a colourless, odourless, tasteless substance, which forms an *acetate*,  $OAc \cdot C_{15}H_{25}O$ , m. p. 79°; the function of the other oxygen atom remains undecided; it does not appear to be ketonic. Oxidation of the alcohol does not lead to definite results.

The residue of the higher-boiling fractions consists of sesquiterpenes, which have not been exhaustively examined. C. S.

**Camomile Oil.** C. HARTWICH and A. JAMA (*Chem. Zentr.*, 1909, 80, [ii], 823; from *Apoth. Zeit.*, 1909, 24, 585—586).—The florets of camomile (*Matricaria chamomilla*) yield 0.35% of a deep blue, viscous volatile oil,  $D^{25}_D$  0.954,  $n^{25}_D$  1.3637344 in alcoholic solution,  $[\alpha]_D = 0$ , saponification value 74.4, which shows no absorption spectrum, and after saponification retains the characteristic odour of camomile. The flower disks yield 0.51% of a slightly green oil,  $D^{25}_D$  0.949,  $n^{25}_D$  1.3637166 in alcohol,  $[\alpha]_D = 0$ , saponification number 33.7, which readily loses its colour and becomes yellow. After saponification, it develops an odour recalling that of lavender oil. It is suggested that camomile oil should be distilled from the florets only, and not from the flower-heads (florets and disks) as at present. T. A. H.

**Composition of Oil of Cloves.** Alcoholic and Aldehydic Constituents. HENRI MASSON (*Compt. rend.*, 1909, 149, 630—632, 795—797).—The following new constituents have been isolated from the fraction of oil of cloves (*Eugenia caryophyllata*) boiling below 125°/10 mm.: Methylamylcarbinol, methylheptylcarbinol, benzyl alcohol, furfuryl alcohol, together with an unsaturated compound, b. p. 190—195°, possibly a methylfurfuryl alcohol.

The fraction of oil of cloves b. p. 65—90°/15 mm. contains small quantities of  $\alpha$ -methylfurfuraldehyde. The fraction having b. p. 105—120°/15 mm. contains a still smaller amount of *dimethylfurfuraldehyde*,  $C_7H_8O_2$ , b. p. 206—208°. This develops an intense violet coloration with  $\alpha$ -naphthol and sulphuric acid, and on oxidation yields *dimethylpyromucic acid*,  $C_7H_8O_3$ , b. p. 129—130°.

Methyl salicylate has been isolated from the fraction of oil of cloves b. p. 105—120°/15 mm. (compare Erdmann, *Abstr.*, 1898, i, 37).

W. O. W.

**Volatile Oils.** ROURE-BERTRAND FILS (*Chem. Zentr.*, 1909, 80, [ii], 1055—1056; from *Wiss. industr. Ber. Roure-Bertrand Fils*, 1909, [ii], 929—944).—Peppermint oil distilled from plants grown at Grasse remained liquid at -17°. Oil prepared in 1907, containing 10.6% combined menthol and 6.4% menthone, was hydrolysed, and

then yielded on fractionation *isovaleraldehyde*, *isoamyl alcohol*, *l-pinene*, a *hydrocarbon*, b. p. 165—167°, *i-cineol*, and *sec.-l-menthol*, as well as *d-menthone*. *Schinus molle* oil is also described (this vol., i, 817).

T. A. H.

**Composition and Fractionation of Samphire Oil.** F. BORDE (*Chem. Zentr.*, 1909, 80, ii, 1335; from *Bull. Sci. Pharm.*, 1909, 16, 393. Compare *ibid.*, 132, and Delépine, this vol., i, 642).—In continuation of previous work (*loc. cit.*), the author finds that the oil distilled from the stems and leaves contains (1) a *terpene*, b. p. 158—160°,  $D_4^{20}$  0.8703,  $[\alpha]_D + 44.37'$ , iodine number 336, which is probably *d-pinene*; (2) a *hydrocarbon* (or a mixture of hydrocarbons),  $C_{10}H_{16}$ , b. p. 176—180°,  $D_4^{20}$  0.8957, iodine number 175.5; (3) a *substance*,  $C_{11}H_{16}O(?)$ , b. p. about 210°,  $D_4^{20}$  0.95023,  $[\alpha]_D + 1.4'$ , iodine number 156, and (4) an *isomeride* of apiole,  $C_{12}H_{14}O_4$ , b. p. 285—295°,  $D_4^{20}$  1.1753,  $[\alpha]_D = 0$ , iodine number 119 (compare Delépine, *loc. cit.*). The quantities of these four products in oils from the fruit, stem and leaf, and the whole plant are given in the original.

T. A. H.

**Main Constituent of Japanese Lac. II. Oxidation of Urushiol Dimethyl Ether by Ozone.** RIKO MAJIMA (*Ber.*, 1909, 42, 3664—3673. Compare this vol., i, 402).—The supposition that urushiol,  $C_{20}H_{30}O_2$ , is a dihydric phenol containing an unsaturated aliphatic group,  $C_{14}H_{25}$ , is more or less supported by the behaviour of urushiol dimethyl ether and ozone in chloroform. When a gas containing 15% of ozone is used at 0°, a very explosive, viscous *tetraozonide*,  $C_{22}H_{34}O_{14}$ , is obtained, in which it is probable that two mols. of ozone have entered the phenolic nucleus, since eugenyl methyl ether under the same conditions yields a *triozonide*,  $C_{11}H_{14}O_{11}$ . When urushiol dimethyl ether is ozonised by 6% ozone, a *diozonide*,  $C_{22}H_{34}O_8$ , or a *triozonide*,  $C_{22}H_{34}O_{11}$ , is obtained, according to the duration of the action. Both of these are decomposed by hot water, yielding carbon dioxide, acetaldehyde, heptaldehyde, azelaic and oxalic acids, and a *substance*,  $C_{15}H_{22}O_3$ , containing two methoxyl groups.

The formation of a triozone suggests that the side-chain may be  $C_{14}H_{23}$ , and contain three double linkings.

*Urushiol diacetate*,  $C_{24}H_{34}O_4$ , is a yellow, viscous liquid, obtained by boiling "urushic acid" with acetic anhydride; it is easily hydrolysed by alcoholic potassium hydroxide.

C. S.

**Extractum Tanacetii.** HERMANN MATTHES and HERMANN SERGER (*Arch. Pharm.*, 1909, 247, 418—431).—In recent years it has been shown repeatedly that the methods of estimating extracts are not satisfactory. The authors select the dried flowers of the tansy and show how the extract, by suitable treatment with alcohol, water, and ether, can be separated into pure resin, resin powder, resin soluble in ether, and fats. The solubilities, colour reactions, acid numbers, ester numbers, saponification numbers, and iodine numbers of these are tabulated.

The resins are separately hydrolysed by alcoholic potassium hydroxide, and thus converted into resin acids soluble in ether, resin acids

insoluble in ether, resin alcohols, and unsaponifiable matter. The fats are examined by the usual methods. A simpler apparatus than Farnsteiner's for the conversion of oleic acid into elaidic acid by a measured quantity of nitrogen peroxide is described and figured.

C. S.

**Soluble Chitin from *Limulus polyphemus*, and its Osmotic Behaviour.** CARL L. ALSBERG and C. A. HEDBLOM (*J. Biol. Chem.*, 1909, 6, 483—497).—Chitin was first separated from the skeletal structures of the king crab (*Limulus*) by Halliburton, and in the present research it was found to have the properties he described, which are the same (percentage composition included) as that from other animals. Prolonged treatment with weak hydrochloric acid in the cold causes it first to gelatinise and then to form a colloidal solution with water. This change cannot be brought about if strong potassium hydroxide is employed in its preparation. The explanation advanced of the colloidal solution is that it combines with solvent water, and is perhaps also hydrolysed. It depresses the freezing point so slightly that its molecular weight is probably very great. It dialyses, and has the peculiar property of carrying the water in which it is dissolved through the membrane.

W. D. H.

**Aloe-Emodin.** OTTO A. OESTERLE and G. RIAT (*Arch. Pharm.*, 1909, 247, 413—417).—The results of previous work (Abstr., 1906, i, 973) indicate that aloetic acid is not, as formerly supposed, tetranitro-anthraquinone, but is nitrated aloe-emodin, probably a mixture of the di- and tri-nitro-derivatives. However, it is oxidised by chromic and acetic acids to a substance, decomposing at about 320°, which is reduced by potassium hydrogen sulphide to a blue substance. By treating a boiling alcoholic suspension of the last with sulphuric acid and sodium nitrite, amino-groups are replaced by hydrogen, and a dihydroxyanthraquinone,  $C_{14}H_8O_4$ , m. p. 190—191° (probably chrysazin), is obtained, which crystallises in glistening, brownish-yellow leaflets and forms an acetate, m. p. 232—234°. Aloe-emodin has been hitherto regarded as trihydroxymethylanthraquinone, but the preceding results confirm Robinson and Simonsen's formula (*Trans.*, 1909, 95, 1085), in which one of the hydroxyl groups is in the side-chain.

C. S.

**Chemical Examination of Elaterium and the Characters of Elaterin.** FREDERICK B. POWER and CHARLES W. MOORE (*Pharm. J.*, 1909, [iv], 29, 501—504).—Elaterium consists of a sediment deposited by the juice of the fruit of the "squirting cucumber" (*Ecballium Elaterium*). Previous work on it has been confined mainly to the isolation and examination of the supposed active principle, elaterin, to which a number of different empirical formulæ have been assigned (compare Berg, Abstr., 1898, ii, 447; 1906, i, 596; 1907, i, 146; 1909, i, 248, 587; Pollak, *ibid.*, 1906, i, 973; von Hemmelmayr, *ibid.*, 1906, i, 973).

Elaterium of English origin contained 5.3% moisture, and yielded, on ignition, 6.7% of ash. It furnished no volatile oil on steam distillation. The portion soluble in boiling water amounted to 6%, and included some starch and dextrose in addition to brown amorphous

matter, devoid of purgative properties. The portion insoluble in water was extracted successively by hot chloroform and alcohol, and in this way 57% of it dissolved. The residue from this treatment was physiologically inert.

The mixed chloroform-alcohol extract was exhausted successively with light petroleum and ether. The residue from this treatment consisted mainly of brown resin. The light petroleum extract gave a small amount of a colourless, crystalline substance, m. p. 170—180°, and, after hydrolysis with potassium hydroxide, a mixture of fatty acids with some phytosterol-like substance. The ether extract consisted mainly of a colourless, crystalline product, m. p. 217—220°, corresponding with the "elaterin" of the Pharmacopœias. This was not homogeneous, but consisted of at least two colourless substances, each crystallising in a different form, neither of which was obtained in an undoubtedly pure state. The one had m. p. 230° (decomp.) and  $[\alpha]_D - 52.9^\circ$ , and the other had a lower melting point and was dextro-rotatory,  $[\alpha]_D + 13.9^\circ$ . Both these substances proved to be of similar empirical composition, but the first was physiologically inert, whilst the second showed marked physiological activity. Examination of "commercial elaterin" showed that this also consisted mainly of varying mixtures of these two substances, and this variation probably accounts for the marked difference in medicinal value of commercial specimens of elaterin.

T. A. H.

**The Chlorophyll Group. IV. Zinc Chlorophyll and Zinc Prophyllotaonin.** HENRYK MALARSKI and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1909, 21, 523—547. Compare this vol., i, 174).—Zinc chlorophylls have been prepared from the chlorophyllans of stinging nettle and maple leaves. These zinc compounds give the Krause reaction, and have spectra similar to that of chlorophyll.

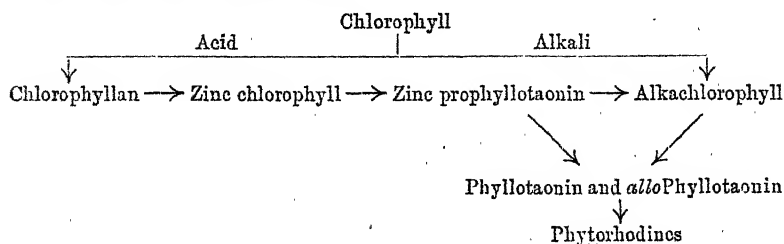
The chlorophyllans are not homogeneous substances; one constituent reacts more readily with zinc hydroxide and carbon dioxide than the other. The former is termed *allochlorophyllan*, and is regarded as a product formed by the action of acids on *allochlorophyll* (Sorby's yellow chlorophyll). When treated with concentrated hydrochloric acid, it yields phylloxanthin as chief product. The function of the carbon dioxide in the formation of the zinc chlorophyll has not been determined; carbon dioxide is not eliminated when the zinc compounds are acidified.

With alkalis the zinc chlorophylls yield two compounds,  $\alpha$ - and  $\beta$ -zinc-prophyllotaonins, which are similar to *allochlorophylls*. The  $\alpha$ -compound reacts with hydrochloric acid, yielding *allophyllotaonin* whereas the  $\beta$ -compound yields *phyllotaonin* together with other substances. With boiling alcoholic hydrochloric acid, the zinc prophyllotaonins yield *phytorhodines*. In the action of alkalis on the zinc chlorophyll, ammonia is not evolved.

It is pointed out that the products obtained by the action of acids on chlorophyll and *allochlorophyll* are different; the former yields chlorophyllan and *allochlorophyllan*, and ultimately *phyllocyanin* and *phylloxanthin*, whereas the latter yields *phyllotaonin* and *allophyllotaonin* and their ethers.

Willstätter's results can be explained by the fact that phyllotaonins are readily converted into phytorhodines.

The following scheme is given :



J. J. S.

**The Chlorophyll Group. V. The Identity of Chlorophyll-pyrrole and Hæmopyrrole.** L. BARABASZ and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1909, 21, 548—550).—The identity of chlorophyll-pyrrole and hæmopyrrole has been established by showing that the former reacts with benzenediazonium chloride, yielding two dyes identical with those obtained from hæmopyrrole (Abstr., 1908, i, 710).

J. J. S.

**The Kaempherol from Robinin.** NICOLAI WALIASCHKO (*Arch. Pharm.*, 1909, 247, 447—462).—The object of the present research is to ascertain whether robigenin, the yellow colouring matter obtained by the hydrolysis of robinin (Abstr., 1904, i, 606), is actually identical with kaempherol, as stated by Perkin (*Trans.*, 1902, 81, 473). This object has been attained, the identity of both substances being proved by a comparison of the tetra-acetates and tetramethyl ethers.

The reaction between kaempherol, ethyl iodide, and potassium hydroxide leads to the formation of *kaempheryl triethyl ether*, m. p. 103—104°.

Kaempherol yields several methylated derivatives. By treatment with methyl iodide and potassium hydroxide, the tetramethyl ether, m. p. 175—176°, and Ciamician and Silber's trimethyl ether, m. p. 139—140°, are obtained, whereas the action of methyl-alcoholic potassium hydroxide and methyl sulphate produces the *dimethyl ether*, m. p. 142—143°, *heptamethyldikaempherol*,  $C_{15}H_5O_6Me_2$ ,  $C_{15}H_5O_6Me_3$ , m. p. 144—145°, and *pentamethylkaempherol*,  $C_{15}H_5O_6Me_5$ , m. p. 155—156°.

When warmed with 12% nitric acid, kaempherol yields 3-nitro-*p*-hydroxybenzoic acid, oxalic acid, and a substance, m. p. 130—131°.

C. S.

**Constitution of Tannin. VI.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1909, 42, 3552—3553).—A reply to Iljin (this vol., i, 503). Tannin, a mixture of digallic and hydroxygallic acids, is decomposed by one of Iljin's methods of purification. *Gallalphenylhydrazone*,  $C_{13}H_{12}O_3N_2$ , from tannin, crystallises in needles, m. p. 172—176°; leucotannin does not yield a phenylhydrazine derivative.

W. R.

**Furfuraldehydephloroglucide.** EMIL VOTOČEK and C. KRAUZ (*Zeitsch. Zuckerind. Böhm.*, 1909, 34, 20).—The author has examined the dark green precipitate obtained when phloroglucinol is added to furfuraldehyde in the conditions obtaining in the well-known Tollens' method for estimating the pentosans. The precipitate has an indefinite composition, constant, however, with definite experimental conditions.

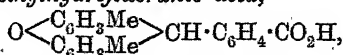
Zinc sulphate considerably retarded the condensation, and it was necessary to heat the mixture to boiling before the reaction was complete. The product was pure yellow in colour, and only took on the ordinary dark green tint after treatment with 12% hydrochloric acid. The yellow substance contained 61.55–62.38% C and 4.01–4.27% H, and the dark green 62.48% C and 4.03% H. Neither substance dissolved in any of the reagents tried.

Ammonium chloride and sodium chloride influence the condensation in the same way; intermediate products with lower carbon content are obtained, which are convertible into the ordinary dark green substance on treatment with acid. E. J. R.

**Pyrone Derivatives.** RUDOLF PUMMERER (*Ber.*, 1909, 42, 3554).—The conclusions drawn by Baly, Collie, and Watson (*Trans.*, 1909, 95, 144) from the absorption spectra of pyrone derivatives are at variance with those derived from the chemical evidence adduced by Willstätter and Pummerer (*Abstr.*, 1904, i, 1043; 1905, i, 457).

W. R.

**Action of Phthalic Anhydride on *m*-Cresol.** WALTHER LAMBRECHT (*Ber.*, 1909, 42, 3591–3595. Compare Bentley, Gardner, and Weizmann, *Trans.*, 1907, 91, 1636).—The chief product obtained by condensing phthalic anhydride with *m*-cresol in the presence of stannic chloride or concentrated sulphuric acid at 120–130° is 3:6-dimethylfluoran, which melts at 213–214° (not 204°). When the fluoran is reduced with potassium ethoxide and zinc dust, the chief product is *dimethylhydrofluoranic acid*,

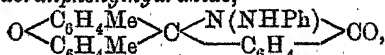


which crystallises from alcohol in small needles, m. p. 232°. When dimethylfluoran, dimethylhydrofluoranic acid, or its salts (silver and calcium) are subjected to destructive distillation, an orange-coloured product is obtained; this is probably O. Weber's 3:6-dimethyl-xanthone (*Abstr.*, 1892, 1093).

Dimethylfluoran does not form salts with hydrochloric, sulphuric, or picric acids, but yields a *stannichloride*,  $\text{C}_{22}\text{H}_{16}\text{O}_3 \cdot \text{HCl} \cdot \text{SnCl}_4$ , in the form of a yellow, crystalline mass.

3:6-Dimethyl dibromofluoran,  $\text{C}_{22}\text{H}_{14}\text{O}_3\text{Br}_2$ , obtained by the action of bromine on a hot solution of dimethylfluoran in glacial acetic acid, crystallises from alcohol in colourless needles, m. p. 330°.

3:6-Dimethylfluoranphenylhydrazide,



crystallises from xylene in colourless, slender needles, m. p. 240°, and

3:6-dimethylfluorananilide,  $C_{28}H_{21}O_2N$ , crystallises from dilute alcohol in colourless prisms, m. p.  $229^{\circ}$ . J. J. S.

**Preparation of 2:3-Diketodihydro-(1)-thionaphthen.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212782). — 2:3-Diketodihydro-1-thionaphthen, m. p.  $118^{\circ}$ , separates in orange-yellow prisms when 2:2-dichloro- or 2:2-dibromo-3-ketodihydro-1-thionaphthen is boiled with water.

2:3-Diketo-5-methyldihydro-(1)-thionaphthen, m. p.  $143-144^{\circ}$ , brown plates, is prepared in a similar manner from 2:2-dichloro- or 2:2-dibromo-3-keto-5-methyldihydrothionaphthen.

5-Chloro-2:3-diketodihydro-(1)-thionaphthen, m. p.  $148-149^{\circ}$ , prepared from 5-chloro-2:2-dibromo-3-ketodihydro-(1)-thionaphthen, crystallises in red plates. When 2:2-dibromo-3-ketodihydrothionaphthen is boiled in alcoholic solution with aniline and sodium acetate, and subsequently acidified, a product is obtained which crystallises in brown, microcrystalline plates. F. M. G. M.

**Preparation of Substituted Halogen Derivatives of 3-Oxy-(1)-thionaphthen.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212942. Compare preceding abstract). — When 3-oxy-(1)-thionaphthen or its homologues are treated with halogens (in the presence or absence of solvents or diluting agents), either mono- or di-halogen substitution products of 3-ketodihydro-(1)-thionaphthen, probably of the general formula  $C_6H_4 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} CR_2$ , are formed ( $R$  = halogen).

2-Bromo-3-ketodihydro-(1)-thionaphthen, m. p.  $89^{\circ}$ , crystallises in colourless prisms.

2-Chloro-3-ketodihydro-(1)-thionaphthen is a red oil with penetrating odour.

2:2-Dibromo-3-ketodihydro-(1)-thionaphthen crystallises in golden-yellow plates, m. p.  $133^{\circ}$ .

2:2-Dichloro-3-ketodihydro-(1)-thionaphthen, a heavy, red oil of characteristic odour resembling that of 2:3-diketodihydro-(1)-thionaphthen, is prepared from 3-oxy-(1)-thionaphthen and sulphuryl chloride.

2:2-Dibromo-3-keto-5-methyldihydro-(1)-thionaphthen, prepared from 3-keto-5-methyl-(1)-thionaphthen, crystallises in golden-yellow needles, m. p.  $99^{\circ}$ .

5-Chloro-2:2-dibromo-3-ketodihydro-(1)-thionaphthen, m. p.  $93^{\circ}$ , is obtained from 5-chloro-3-ketothionaphthen. F. M. G. M.

**Constituents of Meat Extract.** R. KRINBERG (*Ber.*, 1909, 42, 3878—3880. Compare Engeland, this vol., i, 557; Krimberg, *Abstr.*, 1908, i, 842). — Polemical. A claim for priority in establishing the constitution of carnitine. It is agreed that the compound described as oblitine is in reality carnitine ethyl ester. E. F. A.

**Nitrocodeinic Acid, an Oxidation Product of Nitrocodeine and Nitro- $\psi$ -codeine.** FRITZ ACH, LUDWIG KNORR, H. LINGENBRINK, and HEINRICH HÖRLEIN (*Ber.*, 1909, 42, 3503—3510. Compare *Abstr.*, 1903, i, 849). — When nitrocodeine is dissolved in cold

nitric acid (D 1.3) there is produced after a short time a vigorous evolution of gas, and the temperature rises to  $40^{\circ}$ . The mixture, after remaining at the ordinary temperature for four days and then heating for ten hours at  $60^{\circ}$ , is poured into water, when a weakly basic substance is precipitated. The filtrate is neutralised and lead acetate added, when a lead salt is precipitated. The lead is removed by dilute sulphuric acid, and the hot filtrate deposits a resinous mass on cooling; extraction with hydrochloric acid yields *nitrocodeinic acid hydrochloride*, which forms yellow needles. *Nitrocodeinic acid*,  $C_{16}H_{18}O_9N_3$ , purified through its ammonium or barium salt, crystallises in slender needles, decomp.  $300^{\circ}$ . This acid can also be obtained from nitro- $\psi$ -codeine, but not from nitro-oxycodine. Its *potassium* and *barium*,  $C_{16}H_{18}O_9N_3Ba \cdot 2H_2O$ , salts have been prepared, and show it to be dibasic. Its salts with mineral acids are completely dissociated in water.

Aminocodeinic acid is obtained in the form of its *hydrochloride*,  $C_{16}H_{20}O_7N_2 \cdot HCl$ , by reduction with tin and hydrochloric acid. It forms leaflets.

When nitrocodeinic acid is heated at  $140$ – $150^{\circ}$  with hydrochloric acid, *nitronorcodeinic acid*,  $C_{15}H_{16}O_9N_2$ , is obtained in needles. Heating nitrocodeinic acid with hydriodic acid results in the formation of *aminonorcodeinic acid*,  $C_{15}H_{18}O_7N_2$ , as a crystalline powder.

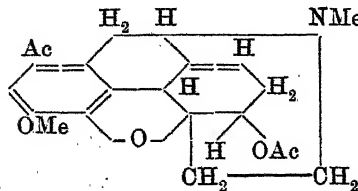
When nitrocodeinic acid is esterified with alcohol and hydrogen chloride, an ester is obtained, but a molecule of water has also been removed. The *methyl* ester,  $C_{17}H_{18}O_8N_2 \cdot 2MeOH$ , forms plates; its *hydrochloride*,  $C_{17}H_{18}O_8N_2 \cdot HCl$ , needles; the *ethyl* ester *hydrochloride*,  $C_{18}H_{20}O_8N_2 \cdot HCl$ , slender needles. Probably a lactone is formed of the nature of betaine.

Diazomethane and nitrocodeinic acid give a *compound*,  $C_{18}H_{20}O_8N_2$  (or  $C_{19}H_{22}O_8N_2$ ), containing three methoxyl groups, which forms yellow prisms, m. p.  $180^{\circ}$ . When this ester is heated with 20% hydrochloric acid, it yields the *hydrochloride*,  $C_{18}H_{20}O_8N_2 \cdot HCl$ , which contains only two methoxyl groups.

W. R.

**Morphine. XX. Acetoxyacetylcodeine.** LUDWIG KNORR, HEINRICH HÖRLEIN, and FRANZ STAUBACH (*Ber.*, 1909, 42, 3511–3521).—The preparation of a triacetylmorphine and diacetylcodeine has been given by Causse (*Abstr.*, 1899, i, 394) and by Knoll & Co. (*Abstr.*, 1907, i, 235).

As morphine contains two hydroxyl groups and codeine only one, this behaviour is surprising, and experiments were undertaken to ascertain the position of the acetyl groups. Causse's results could not be obtained, and are regarded as erroneous, but Knoll & Co.'s were corroborated. As (1) the diacetylcodeine is hydrolysed to a monoacetylcodeine and no further, (2) the latter compound is a ketone, and (3) the morphine alkaloids are derivatives of pyrogallol, the conclusion is drawn that the acetyl group is substituted in benzene nucleus (I) of the codeine, and that the acetoxyacetylcodeine (diacetylcodeine)



has the annexed constitution. This conclusion as to the position of the acetyl group is strengthened by the fact that this compound cannot be nitrated under conditions in which codeine itself is nitrated with ease. Acetoxyacetylcodeine has  $[\alpha]_D^{17} - 207^\circ$  in chloroform solution; the *oxime*,  $C_{22}H_{26}O_5N_2 \cdot \frac{1}{2}EtOH$ , crystallises in needles, m. p. 176—178°.

Hydrolysis of the acetoxyacetylcodeine with sodium ethoxide gives *acetylcodeine*,  $C_{20}H_{28}O_4N_2$ , which crystallises in rectangular plates, m. p. 150°,  $[\alpha]_D^{21} - 141^\circ$ ; the *oxime*,  $C_{20}H_{24}O_4N_2$ , has m. p. 100° (decomp.). *Acetylcodeine methiodide*,  $C_{21}H_{26}H_4NI$ , crystallises in rectangular leaflets, m. p. 235°,  $[\alpha]_D^{15} - 64^\circ$ . When decomposed by boiling sodium hydroxide solution, *acetylmethylmorphimethine*  $C_{21}H_{25}O_4N$ , is formed in 85% yield; it forms needles, m. p. 149°,  $[\alpha]_D^{21} + 150^\circ$ . This compound is not changed by alcoholic potassium hydroxide, and therefore behaves similarly to  $\epsilon$ - and  $\zeta$ -methylmorphimethine, and is distinguished from  $\alpha$ - and  $\gamma$ -compounds, in which a wandering of the ethenoid linking occurs. That the diacetyl compound is a derivative of codeine, and not of  $\psi$ -codeine or *allo-ψ*-codeine, is shown by these compounds also forming isomeric diacetyl compounds with acetic anhydride and sulphuric acid. It is accordingly assumed that the migration of the ethenoid linking occurs during the decomposition of the methiodide, an assumption which is supported by the striking change in the rotation.

*Acetoxyacetylmethylmorphimethine*, prepared by digesting acetylmethylmorphimethine and acetic anhydride for half an hour, is an oily base, which, with methyl iodide, yields the *methiodide*,  $C_{24}H_{30}O_5N$ , separating in yellow crystals, m. p. 180—182°.

When acetylmethylmorphimethine is heated with an alcoholic solution of sodium ethoxide for six hours at 160°, a 75% yield of *acetylmethylmorphol*,  $C_{17}H_{14}O_3$ , is obtained in needles, m. p. 161—162°; its *semicarbazone*,  $C_{18}H_{17}O_3N_3$ , has m. p. 220° (decomp.). The basic product of the above hydrolysis is dimethylaminoethyl ether (compare Abstr., 1904, i, 916).

W. R.

**Morphine. XXI. Acetoxyacetyl Derivatives of *iso*Codeine,  $\psi$ -Codeine, and *allo-ψ*-Codeine.** LUDWIG KNORR, HEINRICH HÖRLEIN, and FRANZ STAUBACH (*Ber.*, 1909, 42, 3521—3522. Compare preceding abstract).—*Acetoxyacetyl-ψ-codeine*,  $C_{22}H_{25}O_5N$ , crystallises in prisms, m. p. 170°,  $[\alpha]_D^{18} - 126^\circ$ . *Acetoxyacetyl*iso*codeine*,  $C_{22}H_{25}O_5N \cdot \frac{1}{2}EtOH$ ,

has m. p. 80—85°; the alcohol-free substance, m. p. 105°,  $[\alpha]_D^{14} - 236^\circ$ . The diacetyl derivative from *allo-ψ*-codeine is an oil. The above compounds are all prepared similarly to that obtained from codeine itself.

W. R.

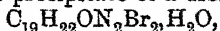
**Constitution of Stachydrine.** R. ENGELAND (*Arch. Pharm.*, 1909, 247, 463—466. Compare Planta and Schulze, Abstr., 1893, i, 447, 679; Jahns, *ibid.*, 1896, i, 712).—Stachydrine closely resembles betaine in its reactions, but differs in yielding dimethylamine by distillation with potassium hydroxide. In this respect it resembles Willstätter's *N*-methylhygric acid (Abstr., 1900, i, 405). The author

shows that the two substances are identical by a comparison of the chlorides, aurichlorides, and platinichlorides. C. S.

### Bromination of Strychnine, Brucine, and other Alkaloids.

JÓZEF BURACZEWSKI and M. DZIURZYŃSKI (*Bull. Acad. sci. Cracow*, 1909, 333—343. Compare Abstr., 1908, i, 1007; this vol., ii, 472).—On adding a solution of bromine in carbon disulphide to a cold saturated alcoholic solution of cinchonine, a bright yellow precipitate is obtained, which readily dissolves in excess of bromine. If the addition of bromine is stopped when a maximum amount of precipitate has been formed, and the latter then collected, a bright yellow tetrabromocinchonine derivative,  $C_{19}H_{22}ON_2Br_2Br_2$ , which is apparently non-crystalline, is obtained, two of the bromine atoms being differently combined from the other two. It is not soluble without decomposition in most organic solvents. Towards acetone it shows a very characteristic behaviour; it first dissolves to a clear yellow solution, and then almost immediately a white, crystalline precipitate forms.

If bromine is added to the alcoholic solution of cinchonine until the precipitate first formed redissolves, and the solution left for some time, a heavy, crystalline precipitate of a dibromo-derivative,



m. p.  $203^\circ$ , is formed, but begins to turn brown above  $190^\circ$ . It is identical with Comstock and König's (Abstr., 1884, 1882; 1886, 281, 1122)  $\alpha$ -cinchonine dibromide, although the melting point is different. When the alcoholic solution is treated with bromine (in carbon disulphide), the tetrabromocinchonine derivative is again produced.

When cinchonine is replaced by quinine and bromine added, a white precipitate of a monobromoquinine,  $C_{20}H_{24}O_2N_2Br$ , is produced, which with excess of bromine yields a yellow pentabromo-derivative,  $C_{20}H_{24}O_2N_2Br_2Br_2Br_2$ . If this yellow product is treated with cold water, in which it is quite insoluble, and then gently warmed (below  $40^\circ$ ), it loses its yellow colour, and a small portion of it dissolves in water. If the liquid is now rapidly filtered and treated with concentrated ammonia, a white, flocculent precipitate is first produced, which almost immediately becomes emerald-green. This substance contains bromine, and is easily soluble in alcohol to a green solution; it is possibly the substance which gives the thalleoquinine reaction.

The authors have previously shown that monobromobrucine dissolves in mineral acids in the cold, forming a red solution. They have now isolated the compound to which the red colour is due, by adding concentrated sulphuric acid, drop by drop, to a mixture of monobromobrucine and water until the acid was in slight excess; on addition of alcohol, a cherry-red precipitate is produced. After purification it is readily soluble in water, and gives a precipitate of barium sulphate on addition of barium chloride; it contains bromine. It could not be further investigated, but was probably the sulphate of monobromobrucine.

If a solution of brucine in dilute nitric acid is added, drop by drop, to absolute alcohol, a cherry-red precipitate is produced of the

formula  $C_{23}H_{26}O_9N_2N_2O_4HNO_3$ . It dissolves readily in water, giving a red solution T. S. P.

**Strychnos Alkaloids. VII. Fission of Brucinonic Acid and of Brucinolone.** HERMANN LEUCHS and L. E. WEBER (*Ber.*, 1909, 42, 3703—3710).—The decomposition of brucinolic acid into glycollic acid and brucinolone by sodium hydroxide (this vol., i, 253) makes it probable that brucinonic acid contains a carbonyl group in the  $\alpha$ -position. If this is so, the acid should lose carbon dioxide by treatment with aniline, and should yield glyoxylic or oxalic acid by fission with sodium hydroxide. Neither of these expectations is fulfilled, since brucinonic acid yields an *anilide*,  $C_{29}H_{29}O_7N_8$ , m. p. 239—240°, when heated with aniline in a current of hydrogen, and is decomposed by alkalis with the formation of glycollic acid. Thus the acid and 1.5 equivalents of *N*-sodium hydroxide at 0° yield glycollic acid and an uncrystallisable product, together with *brucinonic acid hydrate*,

$C_{23}H_{26}O_9N_2$ , m. p. 245°, with previous darkening, which is also produced by the action of boiling 5*N*-hydrochloric acid on brucinonic acid, and is possibly formed by an addition of water, thus:  $:N\cdot CO \rightarrow :NH\cdot CO_2H$ .

The decomposition of brucinolic acid by sodium hydroxide yields a small amount of a *substance*,  $C_{21}H_{24}O_6N_2$ , m. p. 290° (decomp.), which gives the brucine reaction, dissolves in 20% hydrochloric acid and alkali hydroxides, but is insoluble in dilute hydrochloric acid and in sodium carbonate. An isomeric *substance*,  $C_{21}H_{24}O_6N_2$ , m. p. 267—268°, is obtained in the form of the *hydrochloride*,  $C_{21}H_{24}O_6N_2\cdot HCl\cdot \frac{1}{2}H_2O$ , m. p. 245° (decomp.), by treating brucinolone with concentrated hydrochloric acid, at first in the cold and then at 100°.

When brucinolone is treated with 5*N*-nitric acid, carbon dioxide and nitric oxide are evolved, and a *quinone*,  $C_{19}H_{16}O_5N_2$ , m. p. 295° (decomp.), is obtained, which crystallises in large, light red prisms, is decomposed by alkali hydroxides, and is converted by aqueous sulphurous acid at 0° into *bis-desmethylbrucinolone*,  $C_{19}H_{18}O_5N_2$ , which crystallises in yellow prisms and has m. p. 300°, and a small amount of another crystalline substance having the same m. p. The quinol can be re-converted into the quinone by warm dilute or cold concentrated nitric acid. C. S.

**Ketones of the Pyrrolidone Series.** OTTO KÜHLING and L. FRANK (*Ber.*, 1909, 42, 3952—3958).—The interaction of ethyl lævulinate, hydrocyanic acid, and benzylamine in absolute alcoholic solution under pressure yields 2-cyano-1-benzyl-2-methylpyrrolidone, which, when treated according to Blaise's modification (compare Abstr., 1901 i, 133, 252; 1902, i, 164) of the Grignard synthesis,

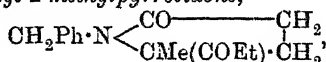
reacts according to the equation:  $CH_2Ph\cdot N \begin{matrix} \text{CO} \\ \text{---} \\ \text{CMe(CN)} \end{matrix} \begin{matrix} \text{CH}_2 \\ \text{---} \\ \text{CH}_2 \end{matrix} + RMgX + H_2O = CH_2Ph\cdot N \begin{matrix} \text{CO} \\ \text{---} \\ \text{CMe(CO}\cdot R) \end{matrix} \begin{matrix} \text{CH}_2 \\ \text{---} \\ \text{CH}_2 \end{matrix} + NH_3 + MgX\cdot OH$ .

The acetyl, propionyl, and benzoyl derivatives thus obtained are extremely stable, and can be heated with concentrated alkali solutions in a reflux apparatus, or with dilute mineral acids in a sealed tube at

150° without decomposing. They exhibit the ordinary reactions for ketones only in a restricted degree, probably owing to the steric hindrance of the pyrrolidone nucleus and the methyl group. The phenylhydrazones and semicarbazones could not be obtained, and the oximes are only obtainable in quantity in presence of excess of potassium hydroxide.

2-Cyano-1-benzyl-2-methylpyrrolidone,  $\text{CH}_2\text{Ph}\cdot\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CMe(CN)} \cdot \text{CH}_2 \end{smallmatrix}$ , m. p. 76—77°, prepared from ethyl lævulate, hydrocyanic acid, and benzylamine, is accompanied by a basic derivative of glutaric acid,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CMe(CN)}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$  (?), which was not obtained sufficiently pure for analysis.

2-Propionyl-1-benzyl-2-methylpyrrolidone,



prepared by the action of magnesium and ethyl iodide on 2-cyano-1-benzyl-2-methylpyrrolidone in ethereal solution, has m. p. 66—67°, and yields an *oxime*,  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_2$ , m. p. 135—136°, which gives the original pyrrolidone derivative, m. p. 66—67°, when heated in a sealed tube with 12% sulphuric acid at 150°.

2-Acetyl-1-benzyl-2-methylpyrrolidone,  $\text{CH}_2\text{Ph}\cdot\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CAcMe} \cdot \text{CH}_2 \end{smallmatrix}$ , forms white, prismatic crystals, m. p. 67—68°; the corresponding *oxime*,  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_2$ , has m. p. 141°.

2-Benzoyl-1-benzyl-2-methylpyrrolidone,  $\text{CH}_2\text{Ph}\cdot\text{N} \begin{smallmatrix} \text{CO} \text{---} \text{CH}_2 \\ \text{CBzMe} \cdot \text{CH}_2 \end{smallmatrix}$ , prepared by the action of magnesium and bromo- or iodo-benzene on 2-cyano-1-benzyl-2-methylpyrrolidine, is obtained as a pale yellow oil which does not solidify; its *oxime*,  $\text{C}_{19}\text{H}_{20}\text{O}_2\text{N}_2$ , has m. p. 218—219°.

T. H. P.

**New Cinchonic Acid Syntheses.** WALTHER BORSCHKE (*Ber.*, 1909, 42, 4072—4088. Compare this vol., i, 52).—When mono-substituted pyruvic acids (for example, phenyl-, *o*-nitrophenyl-, benzoyl-, and benzyl-pyruvic acids) are condensed with an aldehyde and a primary arylamine according to Doebner's method, cinchonic acids are not formed as a rule. Benzylpyruvic acid, however, with aniline and benzaldehyde yields 13% of 2-phenyl-3-benzyleinchonic acid, and with *m*-toluidine and benzaldehyde it yields 18% of 2-phenyl-3-benzyl-7-methyleinchonic acid. The remaining three acids yield under similar conditions diketopyrrolidines. When  $\beta$ -naphthylamine is substituted for the amines of the benzene series, somewhat better yields of cinchonic acids are obtained, for example, phenylpyruvic acid, benzaldehyde, and  $\beta$ -naphthylamine give a 40% yield of 2:3-diphenyl- $\beta$ -naphthyleinchonic acid and no pyrrolidine derivative.

It has also been found possible to condense  $\beta$ -naphthylamine and formaldehyde with the substituted pyruvic acids, yielding substituted naphthaquinoline-4-carboxylic acids.

4:5-Diketo-1:2:3-triphenylpyrrolidine,  $\text{NPh} \begin{smallmatrix} \text{CHPh} \cdot \text{CHPh} \\ \text{CO} \text{---} \text{CO} \end{smallmatrix}$ , ob-

tained by heating an alcoholic solution of aniline, benzaldehyde, and phenylpyruvic acid (Erlenmeyer, Abstr., 1893, i, 36) on the water-bath, crystallises in colourless needles, m. p. 250°. It is feebly acidic, and dissolves to a certain extent in warm sodium hydroxide solution. It does not react with phenylhydrazine, hydroxylamine, or semicarbazide, but yields an *acetyl* derivative,  $C_{22}H_{16}O_2N \cdot Ac$ , m. p. 185°, and a *benzoyl* derivative,  $C_{29}H_{21}O_3N$ , m. p. 174°. When boiled with zinc dust and acetic acid, it is reduced

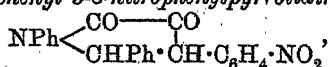
to 4-hydroxy-1:2:3-triphenyl-5-pyrrolidone, 
$$NPh \begin{array}{l} \text{CHPh} \cdot \text{CHPh} \\ \text{CO} - \text{CH} \cdot \text{OH} \end{array}$$
 colourless crystals, m. p. 238°, and when subjected to destructive distillation yields stilbene and a compound,  $C_{21}H_{17}ON$ , m. p. 338°.

4:5-Diketo-2:3-diphenyl-1-o-tolylpyrrolidine,  $C_{23}H_{19}O_2N$ , forms a white, crystalline powder, m. p. 232—234°; the corresponding *m*-tolyl derivative forms an insoluble resin, and the *p*-tolyl compound, colourless crystals, m. p. 224°.

4:5-Diketo-2:3-diphenyl-1-*m*-nitrophenylpyrrolidine,  $C_{22}H_{16}O_4N_2$ , forms yellow needles, m. p. 226°; aniline, formaldehyde, and phenylpyruvic acid yield 4:5-diketo-1:3-diphenylpyrrolidine, m. p. 208°; aniline, *p*-nitrobenzaldehyde, and phenylpyruvic acid yield 4:5-diketo-1:3-diphenyl-2-*p*-nitrophenylpyrrolidine,  $C_{22}H_{16}O_4N_2$ , m. p. 192°; aniline, salicylaldehyde, and phenylpyruvic acid yield 4:5-diketo-1:3-diphenyl-2-o-hydroxyphenylpyrrolidine,  $C_{22}H_{17}O_3N$ , colourless needles, m. p. 252°, and the same acid with aniline and anisaldehyde yields 4:5-diketo-1:3-diphenyl-2-*p*-methoxyphenylpyrrolidine,  $C_{23}H_{19}O_3N$ , m. p. 195°.

Phenylpyruvic acid, benzaldehyde, and  $\beta$ -naphthylamine yield 2:3-diphenyl- $\beta$ -naphthaquinoline-1-carboxylic acid,  $C_{26}H_{17}O_3N$ , in the form of a yellow, crystalline powder, sparingly soluble in the usual solvents. It has m. p. 275°, and is at the same time converted into 2:3-diphenyl- $\beta$ -naphthaquinoline,  $C_{25}H_{17}N$ , which crystallises from aqueous acetone in colourless needles or from ethyl acetate and alcohol in plates, m. p. 179—180°. When acetaldehyde is substituted for benzaldehyde in the above condensation, 2-phenyl-3-methyl- $\beta$ -naphthaquinoline-1-carboxylic acid is obtained in colourless needles, which lose carbon dioxide when heated, yielding 2-phenyl-3-methyl- $\beta$ -naphthaquinoline,  $C_{30}H_{15}N \cdot H_2O$ , m. p. 101°. The nitrate is sparingly soluble, and crystallises in glistening plates. 2-Phenyl- $\beta$ -naphthaquinoline-1-carboxylic acid,  $C_{26}H_{13}O_3N$ , obtained by using formaldehyde, forms colourless, crystalline flocks, and 2-phenyl- $\beta$ -naphthaquinoline,  $C_{19}H_{13}N \cdot 2H_2O$ , colourless needles, m. p. 111°.

4:5-Diketo-1:2-diphenyl-3-o-nitrophenylpyrrolidine,



obtained from *o*-nitrophenylpyruvic acid and benzylideneaniline, crystallises in yellow plates, m. p. 207—208°. The same acid, with benzaldehyde and  $\beta$ -naphthylamine yields 3-phenyl-2-o-nitrophenyl- $\beta$ -naphthaquinoline-1-carboxylic acid,  $C_{26}H_{16}O_4N_2$ , which crystallises in

small, yellow needles; the corresponding base,  $C_{23}H_{10}O_4N_{\frac{1}{2}}H_2O$ , forms yellow plates, m. p. 193—194°.

4:5-Diketo-3-benzoyl-1:2-diphenylpyrrolidine,  $C_{23}H_{17}O_3N$ , prepared from benzoylpyruvic acid, benzaldehyde, and aniline, crystallises from alcohol in colourless needles, m. p. 242—244° (decomp.). With anisaldehyde, 4:5-diketo-3-benzoyl-1-phenyl-2-methoxyphenylpyrrolidine,  $C_{24}H_{19}O_4N$ , m. p. 228°, is obtained. Benzoylpyruvic acid, benzaldehyde, and  $\beta$ -naphthylamine yield 2-benzoyl-3-phenyl- $\beta$ -naphthaquinoline-1-carboxylic acid,  $C_{27}H_{17}O_5N$ , which crystallises in brilliant, colourless needles. When heated, the acid yields 2-benzoyl-3-phenyl- $\beta$ -naphthaquinoline,  $C_{26}H_{17}ON$ , in slender needles, m. p. 185°. When formaldehyde is substituted for benzaldehyde, 2-benzoyl- $\beta$ -naphthaquinoline-1-carboxylic acid is obtained, and this, when heated, yields 2-benzoylnaphthaquinoline,  $C_{20}H_{13}ON$ , as colourless needles, m. p. 108—109°.

4:5-Diketo-1:2-diphenyl-3-benzylpyrrolidine,  $C_{23}H_{19}O_3N$ , colourless needles, m. p. 196°, and 2-phenyl-3-benzylquinoline-4-carboxylic acid,  $C_{23}H_{17}O_3N$ , m. p. 290°, are formed by the action of benzylpyruvic acid on benzaldehyde and aniline, and are readily separated by means of sodium hydroxide solution. 2-Phenyl-3-benzylquinoline,  $C_{22}H_{17}N$ , crystallises in colourless needles, m. p. 96—97°. Benzylpyruvic acid, benzaldehyde, and *m*-toluidine yield 2-phenyl-3-benzyl-7-methylquinoline-4-carboxylic acid,  $C_{24}H_{19}O_3N$ , as colourless needles, which lose carbon dioxide when heated, and then form 2-phenyl-3-benzyl-7-methylquinoline,  $C_{23}H_{19}N$ , m. p. 99°.

Benzylpyruvic acid, benzaldehyde, and  $\beta$ -naphthylamine yield 3-phenyl-2-benzyl-naphthaquinoline-1-carboxylic acid,  $C_{27}H_{19}O_3N$ , which readily loses carbon dioxide, giving the base,  $C_{26}H_{19}N$ , m. p. 152°.

J. J. S.

Synthesis of  $\gamma$ -Coniceine. SIEGMUND GABRIEL (*Ber.*, 1909, 42, 4059—4062).—Previous investigations (Abstr., 1908, i, 649; this vol., i, 491) have shown that when  $\delta$ -phthaliminobutyl methyl ketone and  $\delta$ -phthaliminovaleophenone are hydrolysed, the products are not  $\delta$ -amino-ketones, but the cyclic compounds, 2-methyltetrahydropyridine and 2-phenyltetrahydropyridine, formed by the elimination of water from the  $\delta$ -amino-ketones.

It is now shown that  $\gamma$ -bromopropylphthalimide and sodio-ethyl butyrylacetoacetate react, yielding  $\delta$ -phthaliminobutyl propyl ketone,  $C_8H_4O_2N \cdot [CH_2]_4 \cdot CO \cdot C_3H_7$ , and that when this is hydrolysed, 2-propyltetrahydropyridine ( $\gamma$ -coniceine) is formed (compare V. Braun and Steindorff, Abstr., 1905, i, 812).

J. J. S.

The System Water-Pyridine. ÉMILE BAUD (*Bull. Soc. chim.*, 1909, [iv], 5, 1022—1033).—The conclusions published in the preliminary note (this vol., i, 120) are somewhat modified.

Aqueous solutions of pyridine, on freezing, deposit a mixture of ice and pyridine hydrate until the concentration of pyridine reaches 70%, thence to 85% concentration, pyridine hydrate is deposited, and after that crystals of pyridine. Determinations of the heat of solution of a

mixture of pyridine and water in excess of water indicate the existence of a hydrate,  $C_5H_5N \cdot 2H_2O$ . On these new data, and those recorded formerly (*loc. cit.*), the conclusion is drawn that only one hydrate can be separated from mixtures of pyridine and water, and that this exists in solution and is not merely formed at the moment of crystallisation.

T. A. H.

**Cyanodihydrocyclic Amines. II. Quinoline Series.** ADOLF KAUFMANN and ALBERTO ALBERTINI (*Ber.*, 1909, 42, 3776—3789. Compare this vol., i, 606).—By the action of potassium cyanide on quinoline alkyl halides, cyanodihydroquinolines are obtained, but they differ from the acridine derivatives in being unstable and readily oxidisable, so that they cannot be recrystallised. Oxidation does not result in the loss of the cyano-group, but 4-cyano-1-alkyl-2-quinolones are formed.

For the preparation of 4-cyano-1-methyldihydroquinoline, the reaction between quinoline methiodide and potassium cyanide is carried out in aqueous solution in the presence of ether. The unstable product is dissolved in the ether as it is formed, and may be obtained by evaporation of the solution at the ordinary temperature in the form of rosettes of white needles, m. p.  $86^\circ$ . 4-Cyano-1-ethyldihydroquinoline is obtained similarly; it forms white needles, m. p.  $26^\circ$ . 4-Cyano-1:6-dimethyldihydroquinoline (from 6-methylquinoline) forms white needles, m. p.  $54^\circ$ . 4-Cyano-1:8-dimethyldihydroquinoline crystallises in cubes, m. p.  $79-80^\circ$ . When warmed with alcoholic potassium hydroxide, ammonia is evolved, and a yellow coloration is produced, which afterwards becomes violet. 4-Cyano-1-methyldihydroquinoline is the most stable of these derivatives. On treating the ethereal extract (not the crystallised substance) with an alcoholic solution of picric acid, a red coloration is produced, and quinoline methyl picrate, m. p.  $164-165^\circ$ , is precipitated. From the mother liquor a substance was isolated in small, bright yellow needles, m. p.  $209-210^\circ$ . The cyanodihydroquinolines oxidise spontaneously in the air to form black products, from which pure substances could not be isolated. Attempts to effect the oxidation in alcoholic solution in presence of alkali, or by means of hypobromic acid, hydrogen peroxide, or silver oxide, led to similar results. The cyanoquinolones are prepared by oxidising with air or oxygen in alcoholic solution in the presence of platinised asbestos. 4-Cyano-1-methyl-2-quinolone is a stable substance, forming white, silky needles, m. p.  $165-166^\circ$ . 4-Cyano-1-ethyl-2-quinolone forms pale orange, glistening needles, m. p.  $152^\circ$ . It can also be prepared directly from quinoline ethiodide by dissolving it in methyl alcohol, and treating the boiling solution with potassium cyanide solution while a current of air is driven through the liquid. 4-Cyano-1:6-dimethyl-2-quinolone crystallises in small needles, m. p.  $197-198^\circ$ . 4-Cyano-1:8-dimethyl-2-quinolone forms small laminae, m. p.  $180^\circ$ . Hydrolysis of the cyanoquinolones with alkalis, or, preferably, with acids, yields the 2-quinolone-4-carboxylic acids of Claus, Roser, and Decker. This proves the constitution of the cyanoquinolones. 1-Methyl-2-quinolone-4-carboxylic acid was found to have m. p.

242—243°. The sodium and silver salts were prepared. 1-Ethyl-2-quinolone-4-carboxylic acid was found to have m. p. 202°. The m. p. differ from those previously given for these two compounds. 1:6-Dimethyl-2-quinolone-4-carboxylic acid crystallises in small, bright yellow needles, and has m. p. 287—290°. The distillation of the alkylquinolonecarboxylic acids in a current of hydrogen or carbon dioxide yields the corresponding alkylquinolones. R. V. S.

**Reactions of 2:3:3:5-Tetramethylindolenine.** GIUSEPPE PLANCHER and ORESTE CARRASCO (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 274—278).—This base prepared from methyl isopropyl ketone *p*-tolylhydrazine is, according to Kanschegg (*Abstr.*, 1905, i, 924; 1906, i, 452), 3:3:5-trimethyl-2-methyleneindoline, and forms acetyl and benzoyl derivatives, whilst with nitrous acid it forms a product which gives the reactions of a nitrosoamine. The authors find, however, that the latter compound is, in reality, an oxime (compare *Abstr.*, 1898, i, 536; 1899, i, 543).

The action of benzoyl chloride on 2:3:3:5-tetramethylindolenine in presence of sodium hydroxide yields: (1) a benzoyl derivative,  $C_{19}H_{21}O_2N$ , which forms colourless prisms, m. p. 107°, and (2) a small proportion of a compound,  $C_{19}H_{19}ON$ , which separates in needles, m. p. 158—160°, and is to be investigated later.

The oxime,  $C_{12}H_{14}ON_2$ , obtained by the action of nitrous acid on 2:3:3:5-tetramethylindolenine, forms yellow, acicular crystals, m. p. 214°, and gives no trace of Liebermann's nitrosoamine reaction when pure. The acetyl derivative of the oxime,  $C_{14}H_{16}O_2N_2$ , forms colourless prisms, m. p. 129—130°.

3:3:5-Trimethylindolenine-2-formonitrile,  $C_{12}H_{12}N_2$ , prepared by the vigorous action of acetic anhydride on either the oxime or its acetyl derivative, forms colourless, rhombic plates, m. p. 50—51°, b. p. 144—145°/13 mm. When hydrolysed with alcoholic potassium hydroxide, this nitrile yields two products: (1) a small proportion of the corresponding indolinone (?),  $C_{11}H_{13}ON$ , which crystallises in minute needles, m. p. 81—82°, having the odour of limonene, and (2) an isomeric compound,  $C_{11}H_{13}ON$ , which forms colourless and almost odourless prisms, m. p. 146—147°, and does not give Brunner's indolinone reaction with sulphuric acid and solid dichromate.

3:3:5-Trimethylindolenine-2-formamidoxime,  $C_{12}H_{13}N_2 \cdot NH_2 \cdot OH$ , prepared by the action of hydroxylamine on the formonitrile, forms colourless crystals, m. p. 172—173°. T. H. P.

**Condensation of Esters of Acetonedicarboxylic Acid with Aldehydes by means of Ammonia and Amines.** V. PAVEL PETRENKO-KRITSCHENKO (*Ber.*, 1909, 42, 3683—3694. Compare this vol., i, 605).—The product of the reaction between acetonedicarboxylic ester and an aldehyde in the presence of ammonia or an amine has been shown previously to be a substituted piperidone. The correctness of this constitution is proved by the fact that ethyl 2:6-diphenylpiperidone-3:5-dicarboxylate yields by oxidation an ester, m. p. 195° (*Abstr.*, 1908, i, 564), which is identical with ethyl 2:6-diphenyl-

pyridone-3:5-dicarboxylate, obtained by the action of alcoholic ammonia on Pechmann's ethyl diphenylpyrnedicarboxylate (Abstr., 1891, 673).

[With A. LILIENBLUM.]—Ethyl 2:6-diphenyl-1-methylpiperidone-3:5-dicarboxylate can form, in addition to the ordinary insoluble salts (Abstr., 1907, i, 708), abnormal soluble salts, which are obtained as follows. An alcoholic solution of the base is treated with a few drops of hydrochloric acid, filtered, diluted with water until a turbidity is produced, again filtered, and the filtrate is treated with a platinichloride or a nitrate, whereby a sparingly soluble *platinichloride*,  $(C_{24}H_{27}O_5N)_2, H_2PtCl_6$ , or *nitrate*,  $C_{24}H_{27}O_5N, HNO_3$ , m. p. 137—139°, is obtained.

The benzene mother liquor, from which the hydrochloride of the preceding base has been separated (*loc. cit.*), yields after a few days a second *hydrochloride*, m. p. 153°, from which ammonium hydroxide liberates a *base*,  $C_{24}H_{27}O_5N$ , m. p. 138°, which is stereoisomeric with ethyl 2:6-diphenyl-1-methylpiperidone-3:5-dicarboxylate. The new base, m. p. 138°, forms abnormal soluble salts and a sparingly soluble *nitrite*,  $C_{24}H_{27}O_5N, HNO_2$ , m. p. 108° (decomp.), which responds to Liebermann's reaction and regenerates the unchanged base by treatment with ammonium hydroxide. The hydrochlorides of both bases are oxidised by chromic and acetic acids to ethyl 2:6-diphenyl-1-methylpyridone-3:5-dicarboxylate (this vol., i, 605). The acid obtained by the hydrolysis of this ester decomposes at its m. p., 270°, yielding 2:6-diphenyl-1-methylpyridone,  $NMe \begin{smallmatrix} \text{CPh:CH} \\ \text{CPh:CH} \end{smallmatrix} CO$ , m. p. 176°, which forms a *hydrochloride*, m. p. 245° (decomp.), and a *platinichloride*, m. p. 242—244° (decomp.).

[With Z. HIRSCHBERG.]—The product obtained by the condensation of ethyl acetonedicarboxylate, benzaldehyde, and ethylamine depends on the nature of the solvent. In alcoholic solution, using benzylidene-ethylamine instead of its two components, the main product is a *substance*,  $C_{25}H_{22}O_{10}$ , m. p. 121—123°, which is apparently identical with Knoevenagel's ethyl benzylidenebisacetonedicarboxylate (Abstr., 1896, i, 210), *ethyl 2:6-diphenyl-1-ethylpiperidone-3:5-dicarboxylate*,  $C_{25}H_{20}O_5N$ , m. p. 92° (*hydrochloride*, m. p. 179—181°), being only a by-product. When, however, benzene is used as the solvent, an isomeric *ethyl 2:6-diphenyl-1-ethylpiperidone-3:5-dicarboxylate*, m. p. 137—140° (*hydrochloride*, m. p. 152—153°; *nitrite*, m. p. 118—120°; *platinichloride*), is the sole product. [With B. MALACHOFF.]—The stereoisomerism of the two compounds is proved by the oxidation of their hydrochlorides by chromic and acetic acids to *ethyl 2:6-diphenyl-1-ethylpyridone-3:5-dicarboxylate*,  $C_{25}H_{15}O_5N$ , m. p. 189—190°, which by hydrolysis with alcoholic potassium hydroxide and subsequent acidification yields the *acid*,  $C_{21}H_{17}O_5N$ , m. p. 248—250° (decomp.). The acid forms a *silver salt*,  $C_{21}H_{15}O_5NAg_2$ , yields the preceding ethyl ester, and loses carbon dioxide at its m. p., forming 2:6-diphenyl-1-ethylpyridone,  $C_{19}H_{17}ON$ , m. p. 105—110°.

Mayer's ethyl 1:2:6-triphenylpiperidone-3:5-dicarboxylate is stable to hydrogen chloride in benzene solution, and yields the *hydrochloride*,  $C_{29}H_{29}O_5N, HCl$ , m. p. 145° (decomp.), whereas 1:2:6-

triphenylpiperidone is decomposed under the same treatment, yielding aniline and distyryl ketone.

The mother liquor, from which Mayer's triphenylpiperidone is separated, contains a yellow *isomeride*, m. p. 132°, which also yields aniline and distyryl ketone by treatment with hydrogen chloride, and probably has the constitution:  $\text{NPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$ .

C. S.

**Carbazole Derivatives.** PAUL ZIERSCH (*Ber.*, 1909, 42, 3797—3800).—Carbazole, in suspension in glacial acetic acid at 80°, is easily nitrated by nitric acid (D 1.38). The main product is the 3-nitrocarbazole, m. p. 205°, described by Mazzara and by Votocka, but 1-nitrocarbazole is also formed, crystallising in yellow needles, m. p. 164°. Either nitro-compound is reduced by warming with alcoholic potassium hydroxide and subsequent addition of sodium hyposulphite. 3-Aminocarbazole forms colourless needles, m. p. 240°; 1-aminocarbazole crystallises in snow-white needles, m. p. 230° (decomp.), which are very sensitive to light. The *hydrochloride* and *sulphate* are colourless; the *picrate* forms yellow needles, m. p. 180°; the *benzoate* has m. p. 225°. The *dibenzoate* of diaminocarbazole forms colourless plates, m. p. 270°, which are not sensitive to light.

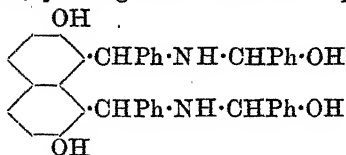
*Dichlorodinitrocarbazole*, produced by the action of chlorine gas on a suspension of dinitrocarbazole in acetic acid, forms yellow needles, m. p. 285°. When reduced in the manner above described, *dichlorodiaminocarbazole* is obtained in yellow flakes; the *sulphate* forms colourless needles, m. p. 320° (decomp.). By the action of fuming nitric acid on carbazole, a tetranitrocarbazole, m. p. 285°, crystallising in bright yellow, rhombic plates, is obtained. This is identical with one of the four products obtained by Ciamician and Silber by the action of fuming nitric acid on acetylcarbazole (*Abstr.*, 1882, 1103). *Tetra-aminocarbazole* was obtained in yellow flakes, which rapidly became black and decomposed. All these aminocarbazole derivatives when diazotised and coupled with naphtholsulphonic acids yield reddish-violet wool dyes.

E. F. A.

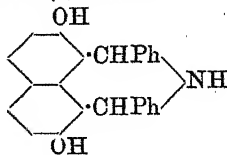
**Condensation of 2:7-Dihydroxynaphthalene with Aromatic Aldehydes and Ammonia. Synthesis of Substituted Acenaphthylenes.** ERICH BESCHKE [with H. RÖLLE and S. STRUM] (*Annalen*, 1909, 369, 157—183).—The condensation of 2:7-dihydroxynaphthalene with ammonia and aromatic aldehydes, particularly benzaldehyde, *p*-methoxybenzaldehyde, *o*-methoxybenzaldehyde, *o*-hydroxybenzaldehyde, *m*-hydroxybenzaldehyde, and furfuraldehyde, has been investigated with the object of obtaining information on the relative reactivity of the two nuclei in 2:7-dihydroxynaphthalene in a reaction characteristic of naphthols (compare Betti, *Abstr.*, 1903, i, 510; 1904, i, 581).

In this particular case it is found that the two nuclei of the naphthalene molecule react in the same manner; the hydrogen atoms in positions 1 and 8 are replaced by organic residues, with the formation of substances which decompose quite readily with ring formation in the peri-position (compare Sachs, this vol., i, 426). For

example, 2:7-dihydroxynaphthalene reacts with ammonia and benzaldehyde, yielding the condensation product (I), which, when boiled



(I.)



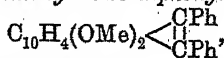
(II.)

with alcohol, water, or aqueous alkali, yields 2:7-dihydroxynaphthylene-1:8-dibenzylideneimine (II) with elimination of 1 mol. of ammonia and 2 mols. of benzaldehyde. The cyclic base is converted by excess of methyl sulphate into the dimethylammonium compound,

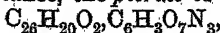
$C_{10}H_4(OMe)_2 \left\langle \begin{smallmatrix} CHPh \\ CHPh \end{smallmatrix} \right\rangle NMe_2 \cdot SO_4Me$ , which, when boiled with an aqueous solution of sodium hydroxide, yields 10-dimethylamino-2:7-dimethoxy-9:10-diphenylacenaphthene,  $C_{10}H_4(OMe)_2 \left\langle \begin{smallmatrix} CHPh \\ CPh \cdot NMe_2 \end{smallmatrix} \right\rangle$  (compare Graebe, Abstr., 1903, i, 408).

Substituted acenaphthylenes are obtained from the aminoacenaphthylenes with the greatest of ease; in order to eliminate, quantitatively, the nitrogen complex as dimethylamine, it is only necessary to heat the tertiary base at its m. p., or boil it for a short time with an acid, preferably glacial acetic acid.

The condensation product of 2:7-dihydroxynaphthalene with benzaldehyde and ammonia,  $C_{38}H_{24}O_2N_2$ , crystallises in colourless, transparent plates, m. p. 125°. 2:7-Dihydroxynaphthylene-1:8-dibenzylideneimine,  $C_{24}H_{19}O_2N$ , crystallises with  $1\frac{1}{2}Et \cdot OH$  in stout, reddish-brown prisms, m. p. 126—127°, and from aqueous acetone in long, yellow needles, m. p. 102—104°, which contain water and acetone in unknown proportions; the base with  $\frac{1}{2}H_2O$  or  $\frac{1}{2}Et \cdot OH$  has m. p. 152—153°; the hydrobromide,  $C_{24}H_{19}O_2N \cdot HBr$ , with  $1H_2O$  forms glistening, golden-yellow crystals, m. p. 228° (decomp.), and with  $1Et \cdot OH$ , pale yellow needles, m. p. 281°; the hydrochloride ( $1H_2O$ ) crystallises in golden-yellow prisms, m. p. 227—228°; the sulphate,  $(C_{24}H_{19}O_2N)_2 \cdot H_2SO_4 \cdot 2H_2O$ , decomposes without melting; the triacetyl derivative,  $C_{30}H_{25}O_5N$ , crystallises in hexagonal plates, m. p. 241—242°; the tribenzoyl derivative,  $C_{45}H_{31}O_3N$ , crystallises in rectangular prisms, m. p. 213°. The substance,  $C_{29}H_{31}O_6NS$ , obtained by the action of methyl sulphate on 2:7-dihydroxynaphthylene-1:8-dibenzylideneimine, crystallises in colourless needles, m. p. 234—235°, and when boiled with a 40% aqueous solution of sodium hydroxide yields 10-dimethylamino-2:7-dimethoxy-9:10-diphenylacenaphthene,  $C_{28}H_{27}O_2N$ , which crystallises in colourless needles, m. p. 173° (decomp.). The latter substance is converted by hot glacial acetic acid into 2:7-dimethoxy-9:10-diphenylacenaphthylene,



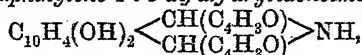
a yellow, crystalline substance, the picrate of which,



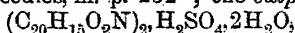
crystallises in reddish-brown, glistening needles with a metallic lustre, m. p. 166°.

The following compounds are prepared by methods similar to those already described.

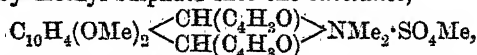
2 : 7-Dihydroxynaphthylene-1 : 8-difurfurylideneimine,



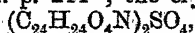
has m. p. 198°; it crystallises with 1Et·OH in colourless prisms, m. p. 198°; the *hydrochloride* (1H<sub>2</sub>O) crystallises in golden-yellow prisms, and turns black at 220°, m. p. 228°; the *hydrobromide* (1H<sub>2</sub>O) forms golden-yellow needles, m. p. 232°; the *sulphate*,



when heated turns black, m. p. 195—196°; the *triacetyl* derivative, C<sub>26</sub>H<sub>21</sub>O<sub>7</sub>N, crystallises in needles, m. p. 228°; the *tribenzoyl* derivative, C<sub>41</sub>H<sub>27</sub>O<sub>7</sub>N, crystallises in rectangular prisms, m. p. 211°. The base is converted by methyl sulphate into the *substance*,



which crystallises in colourless needles, m. p. 215°; the corresponding *chloride*, C<sub>24</sub>H<sub>24</sub>O<sub>4</sub>NCl, forms colourless needles, m. p. 205—206°; the *aurichloride* forms pale yellow crystals, m. p. 158—159°; the *platinchloride* is red, and has m. p. 211°; the crystalline *sulphate*,

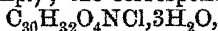


has m. p. 202—203°. 2 : 7-Dimethoxy-9 : 10-difurylacenaphthylene,

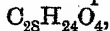
C<sub>16</sub>H<sub>4</sub>(OMe)<sub>2</sub>  $\left\langle \begin{array}{c} \text{C}_4\text{H}_3\text{O} \\ \text{C}_4\text{H}_3\text{O} \end{array} \right\rangle$ , crystallises in dark red leaflets, m. p. 131°; the

*picrate*, C<sub>22</sub>H<sub>16</sub>O<sub>4</sub>·C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub>, forms dark reddish-brown needles with a metallic lustre, m. p. 195°.

2 : 7-Dihydroxy-1 : 8-di-p-methoxybenzylideneimine, C<sub>26</sub>H<sub>23</sub>O<sub>4</sub>N, crystallises in slender, white needles, m. p. 206—207°; the *hydrochloride* has m. p. 258°; the *hydrobromide* (1H<sub>2</sub>O), golden-yellow prisms, has m. p. 265°; the *triacetyl* derivative, C<sub>39</sub>H<sub>29</sub>O<sub>7</sub>N, crystallises with 1Et·OH, m. p. 213—214°. The *substance*, C<sub>31</sub>H<sub>35</sub>O<sub>8</sub>NS, obtained by treating the base with methyl sulphate, crystallises in slender, colourless needles; m. p. 232° (decomp.); the corresponding *chloride*,



forms colourless rhombohedra, m. p. 214—215°; the *aurichloride*, C<sub>30</sub>H<sub>32</sub>O<sub>4</sub>NAuCl<sub>4</sub>, is a pale yellow powder, which decomposes at 120—125°. 2 : 7-Dimethoxy-9 : 10-di-p-anisylacenaphthylene,



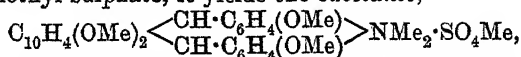
forms glistening, brick-red needles, m. p. 192°; the *picrate* crystallises in dark brown needles, m. p. 184°.

2 : 7-Dihydroxy-1 : 8-di-o-methoxybenzylideneimine, C<sub>26</sub>H<sub>23</sub>O<sub>4</sub>N, crystallises with 1Et·OH, m. p. 266—267°; the *triacetyl* derivative has m. p. 167°. The *substance*, C<sub>31</sub>H<sub>35</sub>O<sub>8</sub>NS, crystallises in small, colourless needles, m. p. 268—269°. 2 : 7-Dimethoxy-9 : 10-di-o-anisylacenaphthylene, C<sub>28</sub>H<sub>24</sub>O<sub>4</sub>, crystallises in glistening, yellow prisms, m. p. 178—179°.

2 : 7-Dihydroxy-1 : 8-di-o-hydroxybenzylideneimine, C<sub>24</sub>H<sub>10</sub>O<sub>4</sub>N, crystallises with 3Et·OH in colourless rhombohedra, m. p. 265—266°; the *hydrochloride* has m. p. 314—315°; the *hydrobromide* (1H<sub>2</sub>O) forms

violet needles, m. p. 307—308°; the *penta-acetyl* derivative has m. p. 219—220°.

2:7-Dihydroxy-1:8-di-*m*-hydroxybenzylideneimine,  $C_{24}H_{19}O_4N$ , crystallises in greyish-white needles, m. p. 195—198°; when treated with excess of methyl sulphate, it yields the substance,



which is converted by aqueous sodium hydroxide into 10-dimethyl-amino-2:7-dimethoxy-9:10-di-*m*-anisylacenaphthene,  $C_{30}H_{31}O_4N$ , crystallising in stellate aggregates of colourless needles, m. p. 164—165°; at this temperature it decomposes into dimethylamine and 2:7-dimethoxy-9:10-di-*m*-anisylacenaphthylene,  $C_{28}H_{24}O_4$ , which crystallises in yellowish-brown, monoclinic prisms, m. p. 146—147°. W. H. G.

[Preparation of Benzoyl-*p*-phenylenediaminesulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 210471).—*p*-Phenylenediaminesulphonic acid reacts readily with benzoyl or the isomeric nitrobenzoyl chlorides in alkaline solution. The products are sparingly soluble powders; they form insoluble diazonium compounds, which yield dyes when combined with naphtholsulphonic acids.

F. M. G. M.

[Preparation of Acyl-3-nitro-*p*-phenylenediamines.] FARBEN-FABRIKEN VORM. F. BAYER & Co. (D.R.P. 211966).—When mono- or di-acyl derivatives of *p*-phenylenediamine (such as formyl, benzoyl, or oxalyl derivatives) are nitrated, the hitherto unknown acyl-3-nitro-*p*-phenylenediamines are produced; these compounds are utilised in the preparation of azo-dyes.

F. M. G. M.

New Phototropic Substances. MAURICE PADOA and F. GRAZIANI (*Atti R. Accad. Lincei*, 1909, [v], 18, ii, 269—273. Compare this vol., i, 676).—Further experiments have been made with the  $\alpha$ - and  $\beta$ -naphthylhydrazones and the *p*-tolylhydrazones of a number of aldehydes, the only general result obtained being that all the  $\beta$ -naphthylhydrazones are phototropic, but none of the  $\alpha$ -naphthylhydrazones. Of fifteen hydrazones examined, eight are more or less phototropic, decolorisation in the dark at the ordinary temperature requiring from a few hours to a few days; the more marked the phototropy, the more rapid is the decolorisation. On heating, decolorisation occurs at temperatures varying from 80° to 145°.

Benzaldehyde- $\alpha$ -naphthylhydrazone is non-phototropic.

Anisaldehyde- $\alpha$ -naphthylhydrazone,  $OMe \cdot C_6H_4 \cdot CH:N_2H \cdot C_{10}H_7$ , forms yellow needles, m. p. 176°, and is not phototropic.

Cuminaldehyde- $\alpha$ -naphthylhydrazone,  $CHMe_2 \cdot C_6H_4 \cdot CH:N_2H \cdot C_{10}H_7$ , forms aggregates of yellow needles, m. p. 159°, and is not phototropic.

Cinnamaldehyde- $\alpha$ -naphthylhydrazone separates as a yellow, crystalline powder, m. p. 165°, and is not phototropic.

Benzaldehyde- $\beta$ -naphthylhydrazone, when exposed to sunlight, becomes pale rose-coloured in two to three minutes; decolorisation takes place either on heating at 120° or after four to five days in the dark.

Anisaldehyde- $\beta$ -naphthylhydrazone, m. p. 176° (Rothenfusser, Abstr., 1908, i, 52, gave 187°), is distinctly phototropic.

Cuminaldehyde- $\beta$ -naphthylhydrazone,  $\text{CHMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N}_2\text{H} \cdot \text{C}_{10}\text{H}_7$ , separates in white leaflets, m. p. 184°, and is phototropic.

Cinnamaldehyde- $\beta$ -naphthylhydrazone separates as a yellow powder, m. p. 193° (Rothenfusser, *loc. cit.*, gave 188°), and is intensely phototropic.

Benzaldehyde- $p$ -tolylhydrazone forms pale yellow, silky needles, m. p. 125° (Reutt and Pawlewski, Abstr., 1904, i, 99, gave 114°, but Schlenk, Abstr., 1908, i, 737, gave 125°), and is coloured red by exposure to sunlight for four to five minutes.

Anisaldehyde- $p$ -tolylhydrazone,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$ , forms lemon-yellow, elongated scales, m. p. 136°, and is not phototropic.

Cinnamaldehyde- $p$ -tolylhydrazone,  $\text{CHPh} \cdot \text{CH} : \text{CH} : \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$ , forms voluminous, canary-yellow needles, m. p. 155°, and is intensely phototropic.

Cuminaldehyde- $p$ -tolylhydrazone,  $\text{CHMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$ , forms pale yellow, voluminous needles, m. p. 137°, and is strongly phototropic; decoloration occurs on heating to about 80°.

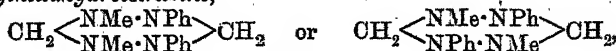
Piperonaldehyde- $p$ -tolylhydrazone,  $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} : \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$ , forms white needles, m. p. 123°, and is intensely phototropic; the colour formed disappears at 110–115°.

$p$ -Tolualdehyde- $p$ -tolylhydrazone,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CH} : \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$ , forms white scales, m. p. 151°, and is not phototropic.

Vanillin- $p$ -tolylhydrazone,  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4\text{Me}$ , crystallises in slender, white needles, m. p. 127°, and is non-phototropic.

T. H. P.

**Hydrazophenylmethyl** [*s*-Phenylmethylhydrazine] from Phenylpyrazole. LUDWIG KNORR and ARNO WEIDEL (*Ber.*, 1909, 42, 3523–3529. Compare Knorr and Köhler, Abstr., 1906, i, 817).—To avoid oxidation during the preparation of *s*-secondary aromatic hydrazines, the 50% potassium hydroxide solution is added slowly to the aqueous solution of 1-phenylpyrazole, through which a current of steam and nitrogen is passed. *s*-Phenylmethylhydrazine, purified from the oxalate, and distilled in a current of nitrogen, has b. p. 110–112°/12–15 mm., 229–230°/738 mm. (compare Abstr., 1906, i, 893),  $D_{15}^{20}$  1.04,  $n_D^{20}$  1.5755, and is very readily oxidised by air to benzeneazomethane. When shaken with formalin and water, *diphenyldimethylhexahydrodrotetrazine*,



is immediately precipitated as a quickly crystallising oil; it crystallises in pearly leaflets from alcohol, m. p. 148°, and this reaction can be used as a test for either the hydrazine or formaldehyde.

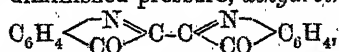
The following salts of *s*-phenylmethylhydrazine are described: hydrochloride, m. p. 160–161°; sulphate; oxalate, m. p. 148°; picrolonate.

Diphenylmethylthiosemicarbazide,  $\text{C}_{14}\text{H}_{15}\text{N}_3\text{S}$ , obtained from the hydrazine and phenylthiocarbimide, has m. p. 175°. *s*-Phenylmethyl-

*hydrazine picrazide*, from picryl chloride and base in alcoholic solution, forms dark red needles, m. p. 172°.

*s*-Phenylethylhydrazine (compare Fischer and Ehrhardt, Abstr., 1880, 243) has b. p. 110°/14 mm., 235—236°/741 mm.,  $n_D^{15}$  1.004,  $n_D^{16}$  1.55; the *hydrochloride* has m. p. 164°; the *oxalate*, 167—168°; the *benzoyl* derivative,  $\text{COPh}\cdot\text{NEt}\cdot\text{NHPh}$ , m. p. 100°. *Diphenylethylthiosemicarbazide*,  $\text{C}_{15}\text{H}_{17}\text{N}_3\text{S}$ , has m. p. 163—164°. *Diphenyldiethylhexahydrotetrazine*,  $\text{C}_{18}\text{H}_{24}\text{N}_4$ , has m. p. 123°. W. R.

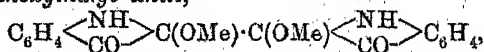
**Dehydroindigotin, a New Oxidation Product of Indigotin.**  
I. LUDWIG KALB (Ber., 1909, 42, 3642—3652. Compare Marchlewski and Radcliffe, Abstr., 1899, i, 74).—When a suspension of very finely-powdered indigotin, lead peroxide, and anhydrous calcium chloride in gently boiling benzene is treated carefully with glacial acetic acid, and, after five minutes, the solution is filtered and concentrated under diminished pressure, *dehydroindigotin*,



is obtained in 60.6% yield. It crystallises in dark yellowish-red, hexagonal plates, dissolves more or less readily in indifferent solvents, and shows a great tendency to regenerate indigotin; this change occurring at 195° [the substance has m. p. 210—215° (decomp.)], or by heating in high-boiling solvents, or by treatment with acids, alkalis, boiling water, stannous chloride, acidified potassium iodide, quinol, phenylhydrazine, and indigo-white. The colour change produced by the reduction of yellow dehydroindigotin to dark blue indigotin is explained by the fact that the process of reduction converts a part of a chromophoric group into an auxochromic group, resulting in a deepening of the colour in accordance with Scholl's generalization (Abstr., 1904, i, 109; 1908, i, 696). When dehydroindigotin, dissolved in an indifferent solvent, is treated with an anhydrous acid, "salts" are produced; in this way a pale yellow diacetate, a yellow *dibenzoate*,  $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2\cdot 2\text{Ph}\cdot\text{CO}_2\text{H}$ , and a yellowish-green *dihydrochloride*,  $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2\cdot 2\text{HCl}$ , have been obtained. The diacetate is identical with oxyacetoin digotin, obtained by O'Neill and formulated as diacetoxindigotin by Marchlewski and Radcliffe (*loc. cit.*). The author inclines to the belief, however, that the acid is attached to the nitrogen atom in these "salts."

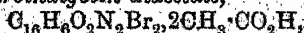
Dehydroindigotin can also be obtained by decomposing a hot mixture of benzene, pyridine, and the diacetate (conveniently obtained by O'Neill's method), or by treating a suspension of indigotin and finely-powdered calcium hydroxide in chloroform with bromine.

*2:2'-Dimethoxyindigo-white*,



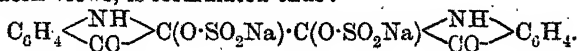
is obtained by the addition of a trace of sodium methoxide to a suspension of dehydroindigotin in methyl alcohol. It crystallises in canary-yellow, hexagonal plates, decomposes at 200°, is stable in hot water, and cannot be reconverted into dehydroindigotin.

*5:5'-Dibromodehydroindigotin diacetate*,



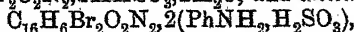
is obtained by the action of potassium permanganate on a suspension of 5:5'-dibromoindigotin in glacial acetic acid. It crystallises in insoluble, yellowish-green prisms, and is decomposed by a boiling mixture of benzene and pyridine, yielding 5:5'-dibromodehydroindigotin m. p. 270° (decomp.), which crystallises in dark reddish-brown leaflets and is stable in hot water. C. S.

**Dehydroindigotin. II. The Hydrogen Sulphite Compounds of Dehydroindigotin and a New Process of Indigo-dyeing.** LUDWIG KALB (*Ber.*, 1909, 42, 3653—3664. Compare preceding abstract).—The most pronounced property of dehydroindigotin is its capability of forming sulphites. The sodium hydrogen sulphite derivative,  $C_{16}H_8O_2N_2 \cdot 2NaHSO_3 \cdot 2H_2O$ , is obtained by shaking powdered dehydroindigotin with a solution of sodium hydrogen sulphite, 38—40° Bé., or by boiling an aqueous alcoholic solution of dehydroindigotin diacetate and sodium sulphite. It separates from water in canary-yellow crystals, has an intensely sweet taste, and, in accordance with modern views, is formulated thus:



From its concentrated aqueous solution, the corresponding potassium derivative,  $C_{16}H_8O_2N_2 \cdot 2KHSO_3 \cdot 2H_2O$ , is obtained by the addition of potassium chloride; it forms yellow crystals, and is less soluble than the sodium compound. The aniline hydrogen sulphite compound,  $C_{16}H_8O_2N_2 \cdot 2(\text{PhNH}_2 \cdot H_2SO_3)$ , is almost insoluble.

The aqueous solution of the sodium compound is decomposed even by sodium carbonate or hydrogen carbonate; sodium hydroxide precipitates indigotin, whilst the solution contains anthranilic acid. Sodium hyposulphite and sodium carbonate, with free access of air or boiling hydriodic acid, convert the sodium compound quantitatively into indigotin. The sodium hydrogen sulphite derivative of 5:5'-dibromodehydroindigotin,  $C_{16}H_6Br_2O_2N_2 \cdot 2NaHSO_3 \cdot 2H_2O$ , is prepared by boiling an aqueous alcoholic solution of sodium sulphite and 5:5'-dibromodehydroindigotin diacetate, or, better, by the addition of bromine, followed by sodium hydrogen carbonate, to a cold aqueous solution of the sodium hydrogen sulphite derivative of dehydroindigotin. In the latter case, the orientation of the halogen atoms is proved by oxidation by potassium dichromate and dilute sulphuric acid, whereby a 60—70% yield of 5-bromoindigotin is obtained. The corresponding potassium derivative,  $C_{16}H_6Br_2O_2N_2 \cdot 2KHSO_3 \cdot 2H_2O$ , and aniline derivative,



are described. By using twice the quantity of bromine in the preceding preparation, the sodium hydrogen sulphite derivative of 5:7:5':7'-tetrabromodehydroindigotin is obtained; it is oxidised by potassium dichromate and sulphuric acid to 5:7-dibromoindigotin. The corresponding potassium and aniline derivatives are mentioned. When a solution of the sodium hydrogen sulphite derivative of tetrabromodehydroindigotin is treated with fuming hydrochloric acid below 0°, the free acid,  $C_{16}H_4Br_4O_2N_2 \cdot 2H_2SO_3 \cdot 14H_2O$ , is obtained in yellow, crystalline plates. The sodium hydrogen sulphite derivative of 5:7:5':7'-tetrachlorodehydroindigotin and the corresponding potassium and aniline

derivatives are obtained by methods analogous to the preceding; the two former contain  $5\text{H}_2\text{O}$ ; the last is anhydrous.

The alkali hydrogen sulphite compounds of dehydroindigotin and its halogenated derivatives are decomposed by boiling dilute hydrochloric acid. The derivatives of the tetrahalogenated compounds are converted almost quantitatively into the tetrahalogenated indigotins, whilst the alkali hydrogen sulphite compounds of dehydroindigotin and of dibromodehydroindigotin yield about 50% of indigotin and dibromoindigotin respectively, the remainder of the materials remaining in the solution as isatin and bromoisatin.

These alkali hydrogen sulphite compounds are sensitive to light. That of tetrabromodehydroindigotin, in particular, is so sensitive that it must be prepared in the dark; paper, soaked in its solution, dried, exposed to sunlight under a negative, and washed, reveals a positive picture.

Silk and cotton, but not wool, can be dyed by immersing the fabric in a solution of the sodium hydrogen sulphite derivative of dehydroindigotin, drying, and treating with dilute mineral acid, alkali hydroxide, or alkali carbonate at  $80-100^\circ$ , whereby indigotin is produced.

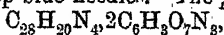
C. S.

**Indigotin. I. Action of Primary Arylamines on Indigotin.** EUGÈNE GRANDMOUGIN and ED. DESSOULAVY (*Ber.*, 1909, 42, 3636—3641).—When indigotin is boiled for some time with a primary arylamine in the presence of boric acid, crystalline products are formed. With aniline, the reaction proceeds according to the equation:  $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2 + 2\text{C}_6\text{H}_5\cdot\text{NH}_2 = \text{C}_{28}\text{H}_{20}\text{N}_4 + 2\text{H}_2\text{O}$ , and the product is regarded as a dianilide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup & \diagdown \\ \text{C}(\text{NPh}) & \text{C}(\text{NPh}) \\ \diagdown & \diagup \\ \text{NH} & \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$ .

The compounds have a deep indigo-blue colour, and are stable towards alkalis. Acids transform them into isomeric, colourless bases, which yield salts of a deep yellow colour. The colourless bases appear to be quindoline derivatives, as they can be decomposed, yielding quindoline (Fichter and Boehringer, *Abstr.*, 1907, i, 92).

The original condensation products, when oxidised with chromic acid, yield isatin, but with nitric acid yield deep red, crystalline compounds.

*Indigotin dianilide*,  $\text{C}_{28}\text{H}_{20}\text{N}_4$ , is obtained by heating together indigotin (1 part), aniline (5 parts), and boric acid (1 part) until when a portion is extracted with alcohol, then dissolved in sulphuric acid, an orange-yellow solution is given. It is usually accompanied by a considerable amount of its leuco-derivative. Alcohol is added, and the solution boiled for half an hour, when the condensation product separates in a crystalline form; it may be recrystallised from pyridine or xylene, and forms deep blue needles. The *picrate*,



crystallises in green needles. *Leucoindigotin dianilide*,  $\text{C}_{28}\text{H}_{22}\text{N}_4$ , is less soluble in xylene, but more soluble in pyridine, than the anilide, and forms colourless needles.

*Indigotin di-p-toluidide*,  $\text{C}_{30}\text{H}_{24}\text{N}_4$ , crystallises from xylene in blue needles. Similar condensation products have been obtained with *o*- and *m*-toluidines, *m*-xylydine, and *adj*-xylydine.

7:7'-Dimethylindigotin also condenses with primary arylamines, and the products yield *o*-methylisatin (Bauer, Abstr., 1907, i, 603) when oxidised.

J. J. S.

**Action of Primary Amines on Indigotin.** EUGÈNE GRANDMOUGIN (*Ber.*, 1909, 42, 4218).—7:7'-Dimethylindigotin (*o*-toluene-indigotin) (preceding abstract) may be characterised by its spectroscopic behaviour. It dissolves in xylene, giving violet-blue solutions, which, for suitable concentrations, exhibit a comparatively sharp absorption line with a band drawn out towards the right; when the solution is diluted with xylene, the line and band disappear. In dilute solution, the absorption line has the wave-length  $\lambda = 603.8$ . Indigotin is less soluble in xylene than 7:7'-dimethylindigotin, and the solution exhibits an absorption band having  $\lambda = 591.4$ . In acetic acid the absorption bands are less sharp and closer together,  $\lambda$  being 615.9 for indigotin and 617.7 for the 7:7'-dimethyl derivative.

T. H. P.

**Pyrimidines. XLVII. Action of Methyl Iodide and of Benzyl Chloride on 6-Methylthiol-4-methyl-2-pyrimidone.** HENRY L. WHEELER and DAVID F. McFARLAND (*Amer. Chem. J.*, 1909, 42, 431—440).—It has been shown in earlier papers that, in general, 2-thiol-6-pyrimidones on alkylation yield both 1- and 3-alkyl derivatives. Recently, however (this vol., i, 677), it has been found that 2-methylthiol- and 2-ethylthiol-4-methyl-6-pyrimidones yield only the 1-alkyl derivatives. It has therefore been considered of interest to study the alkylation of the compound having the opposite configuration, namely, 6-methylthiol-4-methyl-2-pyrimidone, and in this case it has been found that both 1- and 3-derivatives are produced. With methyl iodide, the 1- and 3-isomerides are formed in about equal proportions, whilst with benzyl chloride a larger amount of the 3-derivative is obtained.

6-Chloro-2-methylthiol-4-methylpyrimidine, 
$$\text{N} \begin{array}{c} \diagup \text{C(SMe):N} \\ \diagdown \text{CCl-CH} \end{array} \text{CMe},$$

m. p. 39—40°, obtained by the action of a mixture of phosphoryl chloride and phosphorus pentachloride on 2-methylthiol-4-methyl-6-pyrimidone, forms long needles, and is converted by potassium hydrogen sulphide into 6-thio-2-methylthiol-4-methylpyrimidine,

$$\text{NH} \begin{array}{c} \diagup \text{C(SMe):N} \\ \diagdown \text{CS-CH} \end{array} \text{CMe},$$

m. p. 214°, which crystallises in needles, and when heated above its m. p. undergoes decomposition with formation of 2:6-dithio-4-

methyluracil. 6-Thio-4-methyluracil, 
$$\text{NH} \begin{array}{c} \diagup \text{CO-NH} \\ \diagdown \text{CS-CH} \end{array} \text{CMe},$$
 obtained

by boiling 6-thio-2-methylthiol-4-methylpyrimidine with concentrated hydrochloric acid, forms irregular, yellow prisms, decomposes above 250°, and reacts with methyl iodide in presence of sodium hydroxide to

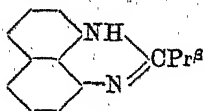
form 6-methylthiol-4-methyl-2-pyrimidone, 
$$\text{N} \begin{array}{c} \diagup \text{CO-NH} \\ \diagdown \text{C(SMe)-CH} \end{array} \text{CMe},$$
 m. p. 174—175°, which crystallises in flat, pale yellow needles. When the

latter compound was treated with benzyl chloride, a product was obtained which could not be purified, but, when heated with concentrated hydrochloric acid, yielded a mixture of 4-methyluracil and its 1- and 3-benzyl derivatives, the last-mentioned compound being obtained in the larger amount; it is therefore inferred that the 3-benzyl compound of the pyrimidone is formed in the larger proportion. By the action of methyl iodide on 6-methylthiol-4-methyl-2-pyrimidone, a mixture of the 3:4- and 1:4-dimethyl derivatives is produced. 6-Methylthiol-3:4-dimethyl-2-pyrimidone, m. p. 170—171°, crystallises in prisms, and when boiled with hydrochloric acid is converted into 3:4-dimethyluracil. The corresponding 1:4-dimethyl compound was not isolated, but was identified by its conversion into 1:4-dimethyluracil.

6-o-Nitrobenzylthiol-4-methyl-2-pyrimidone, m. p. 205°, obtained by the action of o-nitrobenzyl chloride on 6-thio-4-methyluracil, forms clusters of yellow, lancet-shaped crystals. 6-m-Dinitrophenylthiol-4-methyl-2-pyrimidone, m. p. 208°, prepared in a similar manner, crystallises in slender, yellow needles. E. G.

**Cinnoline Compounds.** OSCAR WIDMAN (*Ber.*, 1909, 42, 4216—4217).—A claim for priority (compare Abstr., 1884, 1022) to Stoermer and Fincke (this vol., i, 841) in the preparation of cinnoline derivatives by the diazotisation of an amino-group occupying the ortho-position to an olefinic side-chain. T. H. P.

**Ring Formation in the Peri-Position in the Naphthalene Series.** II. FRANZ SACHS and M. STEINER (*Ber.*, 1909, 42, 3674—3683. Compare this vol., i, 426).—2-isoPropylperimidine (annexed formula),

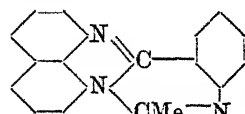


m. p. 87°, crystallises in yellowish-green needles, and is prepared by the interaction of 1:8-naphthylenediamine and isobutyric anhydride; the product is purified by means of the hydrochloride,  $C_{14}H_{15}N_3Cl$ , which decomposes above 260°; the nitrate decomposes at 240°. 2-Butylperimidine,  $C_{15}H_{16}N_2$ , m. p. 165°, is prepared from the diamine and valeric anhydride, and is purified by means of the hydrochloride, m. p. 252—253° (decomp. beginning at 245°). 2-Styrylperimidine, m. p. 136°, is prepared from the diamine and an alcoholic solution of cinnamoyl chloride, and 2-methylvinylperimidine, m. p. 140°, from the diamine and crotonyl chloride in benzene. The chromophoric influence of the ethylenic linking in these two compounds is manifested in the dark red colour of the former and the deep yellow colour of the latter.

2-p-Methoxyphenylperimidine, m. p. 205°, is prepared from 1:8-naphthylenediamine and anisoyl chloride in cold benzene, the resulting hydrochloride being treated with cold ammonium hydroxide. The yield is quantitative when 1:8-naphthylenediamine hydrochloride, suspended in benzene, is boiled with an equal molecular quantity of anisoyl chloride; the hydrochloride has m. p. 280° (decomp. beginning at 260°).

2-o-Nitrophenylperimidine, m. p. 177°, is obtained from o-nitrobenzoyl chloride in cold glacial acetic acid, and crystallises in pale red needles.

Its reduction is difficult, but by means of zinc and 50% acetic acid, 2-*o*-aminophenylperimidine, m. p. 148—150°, can be obtained. 2-*Nitrophenylperimidine*, obtained in a similar manner, crystallises in dark red needles, decomposes at 184°, and is reduced by zinc and 50% acetic acid to 2-*m*-aminophenylperimidine, m. p. 175—180°, which crystallises in reddish-yellow prisms.



2-*p*-Nitrophenylperimidine forms copper-coloured needles, decomposes above 180°, and is reduced to 2-*p*-aminophenylperimidine, m. p. 205° (with previous decomp.), which forms an acetyl derivative,  $C_{19}H_{15}ON_3$ , decomposing above 200°. When 2-*o*-aminophenylperimidine is treated with acetic anhydride, an anhydro-compound, m. p. 139—141° (annexed constitution), is obtained, which separates from 30% alcohol in golden-yellow needles.

A similarly constituted azoimide, containing N in place of CMe, is obtained by diazotising 2-*o*-aminophenylperimidine in cold acetic acid; it is a dark red substance, which decomposes explosively at 140°.

C. S.

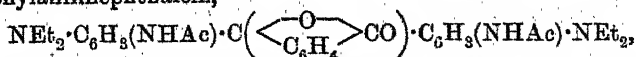
**Oxidation of Dimethylanilinoisatins.** N. DANAILA (*Compt. rend.*, 1909, 149, 793—795. Compare Abstr., 1907, i, 976).—It has already been shown from a study of their oxidation products that phenolisatin and its derivatives are derivatives of *o*-aminobenzaurin and not of an *o*-aurin. The malachite-greens produced by the oxidation of Baeyer's dimethylanilinisatin (Abstr., 1886, 155) and of its nitro-, chloro-, bromo-, dichloro-, and dibromo-derivatives have now been studied in the same way, and the results found to confirm the theory previously advanced.

The acetyl derivative of dimethylanilinisatin has m. p. 179—180°. The compounds obtained by oxidising the substituted dimethylanilinisatins with lead peroxide are green, crystalline substances analogous to the malachite-greens. The results of analyses agree more closely with the formulæ of *p*-hydroxy-*o*-aminomalachite-greens,  $C_{23}H_{25}ON_3$ ,  $C_{23}H_{24}ON_3X$ ,  $C_{23}H_{22}ON_3X_2$ , than with those of the corresponding *o*-amino-compounds.

The constitution of the unsubstituted green base is considered to be best represented by the annexed formula.

W. O. W.

**Flaveosines.** EUGÈNE GRANDMOUGIN and ARNOLD LANG (*Ber.*, 1909, 42, 4014—4019. Compare D.R.-P. 49850).—Acetyldiethyl-*m*-phenylenediamine,  $NHAc \cdot C_6H_4 \cdot NEt_2$ , separates from aqueous alcohol in colourless crystals, m. p. 73°, and when heated with phthalic and acetic anhydrides for five hours at 150° yields diacetyldiamino-diethylanilinephthalein,



which forms colourless, stable crystals, m. p. 246°. The condensation product, when boiled for some time with 20% hydrochloric acid, yields 2:7-tetraethyldiamino-9-phenylacridine-2'-carboxylic acid (tetra-

ethylflaveosine),  $\text{NEt}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \diagup \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}) \diagdown \end{array} \text{C}_6\text{H}_3 \cdot \text{NMe}_2$ , which crystallises from alcohol in orange-yellow needles, m. p.  $333^\circ$ . When freshly precipitated, the dye is soluble in dilute sodium hydroxide solution, but is precipitated on the addition of acetic acid. Its solution in concentrated sulphuric acid has a pale yellow colour with a bluish-green fluorescence, and, when diluted, has a deep red colour with a pale brown fluorescence. It forms well-defined salts; the following have been prepared and analysed: *picrate*,  $\text{C}_{28}\text{H}_{31}\text{O}_2\text{N}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , m. p.  $268^\circ$ ; *hydrochloride*,  $\text{C}_{28}\text{H}_{31}\text{O}_2\text{N}_3 \cdot 2\text{HCl}$ ; *zincchloride*,  $2\text{C}_{28}\text{H}_{31}\text{O}_2\text{N}_3 \cdot 2\text{HCl} \cdot \text{ZnCl}_2$ ; *mercurichloride*,  $\text{C}_{28}\text{H}_{31}\text{O}_2\text{N}_3 \cdot 2\text{HCl} \cdot 2\text{HgCl}_2$ , and *platinichloride*.

The *ethyl ester*,  $\text{C}_{30}\text{H}_{35}\text{O}_2\text{N}_3$ , prepared with the aid of alcoholic hydrogen chloride, crystallises from a mixture of alcohol and benzene in orange-yellow needles, m. p.  $248^\circ$ . The *hydrochloride* forms brilliant red needles, and the *picrate*, orange-red crystals, m. p.  $227^\circ$ . The ester when brominated in alcoholic solution yields a *tetrabromo-derivative* which crystallises in red needles, m. p.  $167^\circ$ .

*Tetramethylflaveosine*, obtained from *acetyltrimethyl-m-phenylenediamine*, m. p.  $87^\circ$ , crystallises from glacial acetic acid in orange-coloured prisms, which are not molten at  $360^\circ$ . Its acetic acid solution imparts to silk a yellow colour with a green fluorescence. Its *tetrabromo-derivative*,  $\text{C}_{34}\text{H}_{19}\text{O}_2\text{N}_3\text{Br}_4$ , separates from alcohol in reddish-brown crystals, m. p. above  $360^\circ$ .

The *ethyl ester* of tetramethylflaveosine forms reddish-brown needles, m. p.  $350^\circ$ , and reacts with a nitrobenzene solution of methyl sulphate, yielding the *acridinium methyl sulphate* derivative of the ester,  $\text{C}_{28}\text{H}_{23}\text{O}_6\text{N}_3\text{S}$ , which crystallises from alcohol and benzene in brownish-violet needles, m. p.  $268^\circ$ . Most of the flaveosines and their derivatives give well-defined absorption spectra.

Phthalanil derivatives are formed in the preparation of the flaveosines, and can be used for characterising *as-dialkylphenylenediamines*.

*Dimethyl-m-aminophthalanil*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_4$ , is best prepared by heating an alcoholic solution of dimethyl-*m*-phenylenediamine and phthalic anhydride with sodium acetate. It crystallises from alcohol in colourless needles, m. p.  $144^\circ$ . The corresponding *diethyl* compound,  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2$ , forms pale yellow needles, m. p.  $120^\circ$ .

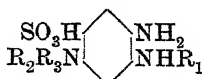
*Dimethyl-p-aminophthalanil*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CO}$ , forms yellow needles, m. p.  $255^\circ$ , and the corresponding *diethyl* compound, deep yellow needles, m. p.  $217^\circ$ .

*Diacetyltrimethyl-m-phenylenediamine*,  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_3$ , separates from alcohol in colourless crystals, m. p.  $69^\circ$ , and does not yield a flaveosine with phthalic anhydride.

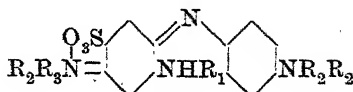
J. J. S.

**Preparation of Safraninesulphonic Acids.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 212472).—1:2:4-Triaminobenzene-5-sulphonic acids of the type (I), where  $\text{R}_1$  is an alkyl, arylalkyl, or

aryl group;  $R_2$  and  $R_3$ , hydrogen, similar or different alkyl, arylalkyl, or aryl groups, are condensed with aromatic amines, and the resulting indamines (II) oxidised to safranines.

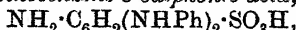


(I.)



(II.)

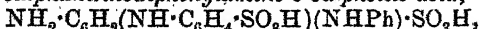
1-Amino-2:4-dianilinobenzene-5-sulphonic acid,



is prepared by heating sodium 2:4-dichloro-1-nitrobenzene-5-sulphonate with aniline at 120—150°, and subsequent reduction of the resulting nitrodianilinobenzenesulphonic acid.

Sodium 5-chloro-2-nitrodiphenylamine-4-sulphonate, yellow crystals, is formed when sodium 2:4-dichloro-1-nitrobenzene-5-sulphonate is heated with aniline in the presence of sodium acetate. This substance, after heating with 20% ammonium hydroxide, at 150°, during five hours, yields sodium 2-nitro-5-aminodiphenylamine-4-sulphonate, crystallising in glistening leaflets; on subsequent reduction, it gives 2:5-diaminodiphenylamine-4-sulphonic acid, colourless, glistening leaflets; the alkaline solution becomes violet on exposure to air, whilst the acid solution oxidises to a blue liquid.

4-Amino-3-sulphanilinodiphenylamine-5-sulphonic acid,



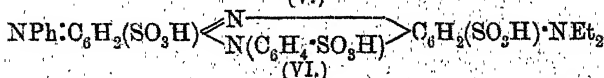
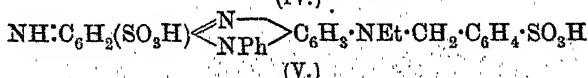
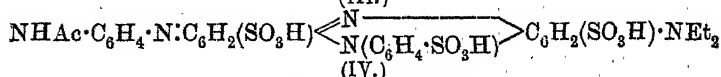
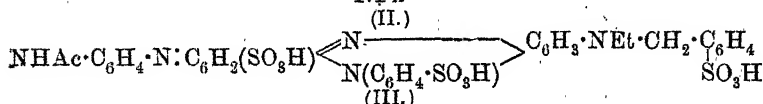
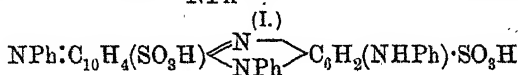
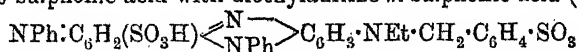
is prepared as follows: sodium *m*-dichloronitrobenzenesulphonate, sodium aniline-*p*-sulphonate, and sodium carbonate are heated together in aqueous solution during fifteen hours. The yellow, crystalline condensation product separates on cooling, and, after heating at 140—150° with aniline, yields 4-nitro-3-sulphanilinodiphenylamine-6-sulphonic acid, yellow crystals; the sparingly soluble potassium salt crystallises in slender needles; on reduction, this acid yields the amino-acid mentioned previously.

When the condensation product from *m*-dichloronitrobenzenesulphonic acid and aniline-*p*-sulphonic acid is boiled in aqueous solution with *p*-phenylenediamine and potassium carbonate, potassium 1-nitro-2-sulphanilino-4-aminoanilinobenzene-5-sulphonate (reddish-brown crystals) is produced; this yields an acetyl derivative, the potassium salt of which crystallises in red needles, and on reduction yields 1-amino-2-sulphanilino-4-acetylaminoanilinobenzene-5-sulphonic acid,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H})(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}) \cdot \text{SO}_3\text{H}$ , colourless needles from water.

Details of preparation and properties of the dyes prepared from the following compounds are given in the patent. 1-Amino-2:4-dianilinobenzene-5-sulphonic acid condenses with ethylbenzylanilinesulphonic acid (I) and with phenyl- $\alpha$ -naphthylamine-6(or 7)-sulphonic acid (II).

1-Amino-2-sulphanilino-4-acetylanilinobenzene-5-sulphonic acid with ethylbenzylanilinesulphonic acid (III) with diethylaniline-*m*-sulphonic acid (IV). 2:5-Diaminodiphenylamine-4-sulphonic acid with ethyl-

benzylanilinesulphonic acid (V). 4-Amino-3-sulphanilindiphenylamine-6-sulphonic acid with diethylaniline-*m*-sulphonic acid (VI):



F. M. G. M.

**Amino-derivatives of Phenylauramines and of Rheonine.** EUGÈNE GRANDMOUGIN and ARNOLD LANG (*Ber.*, 1909, 42, 3631—3635).—A number of *m*-aminoauramines have been prepared in order to determine their relationship to the *rheonines* (D.R.-P. 82989).

*m*-Aminophenylauramine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , obtained by heating auramine base with *m*-phenylenediamine at  $140^\circ$  in a current of hydrogen until ammonia ceases to be evolved, crystallises from alcohol in pale yellow prisms, m. p.  $198^\circ$ . Salts cannot be obtained in aqueous solution, as the addition of acids brings about hydrolysis. The *picrate*,  $\text{C}_{23}\text{H}_{26}\text{N}_4\text{C}_6\text{H}_5\text{O}_7\text{N}_3$ , has m. p.  $198^\circ$ .

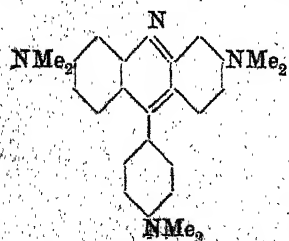
*m*-Dimethylaminophenylauramine,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , forms pale yellow crystals, m. p.  $180^\circ$ ; the orange-red *picrate* has m. p.  $151^\circ$ . The corresponding *diethyl* compound,  $\text{C}_{27}\text{H}_{34}\text{N}_4$ , has m. p.  $157^\circ$ .

2-Amino-*p*-tolylauramine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , obtained from auramine and *m*-tolylenediamine, separates from a mixture of benzene and alcohol in pale yellow prisms, m. p.  $229^\circ$ . *Dimethyl-p*-aminophenylauramine,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , forms deep

yellow crystals, m. p.  $179^\circ$ , and the corresponding *diethyl* compound,  $\text{C}_{27}\text{H}_{34}\text{N}_4$ , has m. p.  $142^\circ$ , and its *picrate*, m. p.  $217^\circ$ .

*m*-Aminoauramines, when heated with zinc chloride, yield acridine derivatives, whereas phenylauramine and its *p*-amino-compounds do not.

2:8:4'-Hexamethyltriamino-5-phenylacridine (hexamethylrheonine) (annexe formula) is obtained from *m*-dimethy



aminophenylauramine and zinc chloride at 200—210° in the form of the zinc chloride,  $C_{25}H_{28}N_4 \cdot 2HCl \cdot ZnCl_2 \cdot 3H_2O$ . The base,  $C_{25}H_{28}N_4$ , forms brown crystals, m. p. 285°, and dissolves in acids, yielding deep red solutions.

J. J. S.

**Aniline-black. III.** RICHARD WILLSTÄTTER and STEFAN DOROGI (*Ber.*, 1909, 42, 4118—4135. Compare Abstr., 1907, i, 641; this vol., i, 535).—The aniline-black richest in hydrogen is a trebly quinonoid derivative of the leuco-base of the formula  $C_{48}H_{36}N_8$ . It is possible to prepare aniline-blacks containing less hydrogen, and even those containing oxygen. The base of the least oxidised dye is blue, forms green salts; and is turned light green by sulphurous acid. The most oxidised product is deep black, and not affected by sulphurous acid. The trebly quinonoid aniline-black previously described (this vol., i, 535) can also be prepared by oxidation with chlorate or persulphate in the cold, less than the calculated quantity of oxidising agent being used. This can be further oxidised by hydrogen peroxide to the *quadruply quinonoid aniline-black*,  $C_{48}H_{34}N_8$ :

$NPh \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot NH$ .  
The new compound is a darker blue-black, and the salts are dark green; sulphurous acid has relatively little influence. The trebly quinonoid substance unites with 4HCl, all of which are displaced by ammonia. The quadruply quinonoid, however, only adds about  $2\frac{1}{2}$ HCl, one of which enters the nucleus, forming a chlorinated aniline-black base. The quadruply quinonoid compound is formed from aniline when an excess of the oxidising agent is employed; thus it is formed in Green's process of oxidation in presence of copper sulphate and *p*-phenylenediamine. It is most conveniently obtained by oxidation with chlorate in the cold. The "copper sulphate chlorate black" of Müller and Nietzki, and the "vanadium chlorate black" of Keyser, represent the same substance containing some chlorine.

Preparations obtained by these various methods agree in that (1) they are almost quantitatively oxidised to quinone, (2) one-eighth of the nitrogen is eliminated as ammonia, (3) they form a chlorine compound with 4.5% chlorine.

The trebly quinonoid black is hydrolysed by heating in sealed tubes at 200° to  $C_{48}H_{35}ON_7$ ; the base is dull black with a blue shade; the salts are greenish-black. Sulphurous acid turns the base greenish-black. Both when these compounds are further oxidised, or when the quadruply quinonoid aniline-black is hydrolysed, the aniline-black,  $C_{44}H_{33}ON_7$ :

$NPh \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot N \cdot C_6H_4 \cdot O$ , is formed. Both base and salts are of the same dull black colour, which is unchanged by sulphurous acid. It is possible to produce this hydrolysed quadruply quinonoid black from aniline salts in one operation when an excess of strong oxidising agents is employed.

The historic emeraldine described by Crace Calvert, Lowe, and Clift is in reality the trebly quinonoid aniline-black. The name emeraldine was also assigned by Caro to the phenylquinonedi-imine subsequently prepared by Willstätter and Moore, which has the

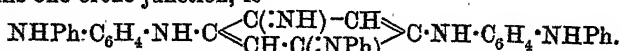
formula  $\text{NHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}_6\text{H}_4 : \text{NH}$ , and differs from aniline-black in being easily soluble in chloroform, forming reddish-violet solutions, and in being decolorised by ammonium sulphate. It is proposed to abandon the name emeraldine for the trebly quinonoid aniline-black, and restrict its use to the polymeride of phenylquinone-di-imine. These results afford a complete explanation of the processes in the technical preparation of aniline-black.

E. F. A.

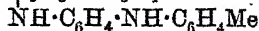
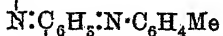
**Polymerisation of Quinoned-di-imines.** RICHARD WILLSTÄTTER and HEINRICH KUBLI (*Ber.*, 1909, 42, 4135—4151).—Benzoquinone-phenyldi-imine is easily condensed to a blue bimolecular product, the emeraldine of Willstätter and Moore (*Abstr.*, 1907, i, 641, and preceding abstract), which may either possess an indamine or anilinoquinone constitution. To settle this structure the condensation of benzoquinonephenyldi-imines, substituted in the para-position, benzoquinonetolyldi-imine, and benzoquinoneanisyl-di-imine has been studied. These substituted imines are deeper in colour than benzoquinone-phenyldi-imine; the salts of the tolyl derivative give red, of the anisyl derivative violet, solutions. These imines are unable to polymerise to emeraldine, but they are polymerised in quite another manner by the action of hydrogen chloride on their solution in methyl alcohol, when much of the corresponding aminodiphenylamine is present. Red-coloured termolecular imines are formed, which do not alter in colour on mild oxidation, are not hydrolysed to benzoquinone, and are not further condensed to aniline-black. A similar termolecular amine is yielded by benzoquinonephenyldi-imine.

In reality the reaction consists in a condensation of imine with amine to form a leuco-compound, which has a reducing action on a further molecule of imine.

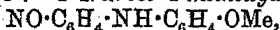
Emeraldine, when oxidised with chromic acid, gives only three-fourths of the theoretical quantity of benzoquinone; when lead peroxide is used, 94% of the theoretical quantity is obtained. The new termolecular compound when oxidised only yields benzoquinone from five of the six aryl groups. Accordingly, emeraldine only contains para-junctions, and the constitution of the new compound, which contains one ortho-junction, is



The tolyl derivative contains only one benzene nucleus, which forms a quinone (annexed formula).



4-Methoxydiphenylamine, prepared by methylation of *p*-hydroxydiphenylamine with methyl sulphate, forms thin, glistening prisms, m. p. 105° (corr.), b. p. 195°/12 mm. The nitrosoamine forms bright yellow prisms, m. p. 83°. 4-Nitroso-4-methoxydiphenylamine,



formed by the internal rearrangement of the nitrosoamine, separates

in prisms with a steel-blue lustre, but appearing olive-green or brown by transmitted light; m. p.  $165^{\circ}$  (corr.). It forms the 4'-amino-4-methoxydiphenylamine, m. p.  $102^{\circ}$ , b. p.  $238^{\circ}/12$  mm., described by Jacobson, Jaenicke, and Meyer (Abstr., 1897, i, 143) on reduction.

*p*-Benzoquinone-*p*-anisyl-di-imine,  $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , forms rosettes of glistening, flat prisms of golden-yellow colour, which becomes ochre-yellow when they are powdered, m. p.  $71-72^{\circ}$ . It forms a dark blue solution in concentrated sulphuric acid. The monohydrate is lighter in colour, m. p.  $49^{\circ}$ .

*p*-Benzoquinone-*p*-anisylmonoimine,  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , obtained on keeping the di-imine in aqueous solution, forms rhombic plates, m. p.  $84^{\circ}$ , with a green shimmer and a bluish-brown red powder.

*p*-Benzoquinone-*p*-tolyl-di-imine,  $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared by oxidation of *p*-aminophenyl-*p*-tolylamine by means of silver oxide in ethereal solution, forms brownish-yellow prisms, m. p.  $114^{\circ}$ . *p*-Benzoquinone-*p*-tolylmonoimine,  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , forms bright, reddish-brown, four-sided prisms, m. p.  $83-83.5^{\circ}$ . The mono- and di-hydrochlorides form reddish-brown powders, and, after drying, dissolve in water, alcohol, or acetone, giving red solutions. *p*-Benzoquinonetolyl-di-imine, when reduced with stannous chloride, changes from red to blue, and then becomes decolorised. On the other hand, the salts of amino-methoxydiphenylamine, when oxidised with successive small quantities of bromine, become at first blue and finally violet; the corresponding tolyl compounds become first blue and then red on oxidation.

The termolecular *p*-benzoquinonephenyl-di-imine,  $\text{C}_{36}\text{H}_{30}\text{N}_6$ , crystallises in rhombic plates, m. p.  $217-218^{\circ}$  (corr.); the monohydrochloride is a blue powder, giving blue solutions; the dihydrochloride, a green powder, forming bluish-green solutions in acetone and alcohol.

The termolecular *p*-benzoquinonetolyl-di-imine,  $\text{C}_{39}\text{H}_{36}\text{N}_6$ , crystallises in lustrous, copper-like, light reddish-brown prisms, which soften at  $180^{\circ}$ , m. p.  $187^{\circ}$  (corr.). It forms carmine-red solutions, but dissolves in acetic acid with a blue coloration. The monohydrochloride is blue; the dihydrochloride, dark green.

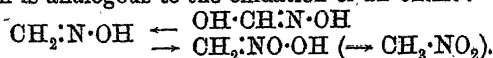
Termolecular *p*-benzoquinoneanisyl-di-imine,  $\text{C}_{39}\text{H}_{36}\text{O}_2\text{N}_6$ , forms chocolate-brown prisms, which darken at  $150^{\circ}$ , and soften at  $170^{\circ}$ , m. p.  $176^{\circ}$ .

On oxidation of equimolecular proportions of *p*-hydroxydiphenylamine and *p*-aminophenyl-*p*-tolylamine with hydrogen peroxide, the leuco-base,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , is obtained, crystallising in colourless plates, m. p.  $211-212^{\circ}$ . This, when further oxidised, yields the homologue of the red imine described by Willstätter and Moore (*loc. cit.*), namely,  $\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{O}$ ; it crystallises in red aggregates of pointed crystals, m. p.  $205-206^{\circ}$ .

The corresponding leuco-base from 4'-amino-4-methoxydiphenylamine forms colourless plates, m. p.  $189-190^{\circ}$ ; the red imine crystallises in pointed prisms, m. p.  $229-230^{\circ}$ . E. F. A.

**Oxidation of Normal Diazohydroxides with Hydrogen Peroxide.** EUGEN BAMBERGER and OSCAR BAUDISCH (*Ber.*, 1909, 42, 3568-3582. Compare Abstr., 1893, i, 326-327; 1894, i, 412).—When a strongly alkaline solution of a normal diazohydroxide is

oxidised with hydrogen peroxide at low temperatures ( $-6^{\circ}$ ), the products obtained are the alkali salts of a benzenediazoic acid and of a nitrosophenylhydroxylamine:  $\text{Ar}\cdot\text{N}\cdot\text{N}\cdot\text{O}\cdot\text{Na} \begin{matrix} \leftarrow \text{Ar}\cdot\text{N}\cdot\text{NO}\cdot\text{O}\cdot\text{Na} \\ \leftarrow \text{O}\cdot\text{NAr}\cdot\text{N}\cdot\text{O}\cdot\text{Na} \end{matrix}$ , a reaction which is analogous to the oxidation of an oxime:



In the case of sodium *p*-chlorodiazobenzene oxide, it has been found possible to isolate both oxidation products together with *p*-dichloroazobenzene and a compound, m. p.  $135\cdot5-136^{\circ}$ , which is probably dichloroazoxybenzene, but with diazobenzene hydroxide the amount of nitrosohydroxylamine is so small that its formation has been merely confirmed; it was not found possible to isolate the pure compound.

Previous experiments on the oxidation of diazobenzene hydroxide have shown that nitrosobenzene is sometimes formed. This compound is now regarded as a secondary product formed by the decomposition of the nitrosohydroxylamine,  $\text{O}\cdot\text{NPh}\cdot\text{N}\cdot\text{O}\cdot\text{Na}$ , since this latter is readily transformed by alkaline oxidising agents (Abstr., 1898, i, 367) into nitrosobenzene and an alkali nitrite. This reaction does not occur when alkaline hydrogen peroxide is used; the oxidation then stops at the formation of the aryl nitrosohydroxylamine.

It is shown that nitrosobenzene cannot be obtained by the oxidation of benzenediazoic acid, and also that the diazoic acid and nitrosohydroxylamine cannot be transformed into each other.

The diazo-compounds are not oxidised by hydrogen peroxide in the presence of a very large excess of alkali, and isodiazohydroxides appear to be stable towards alkaline hydrogen peroxide.

The author is of opinion that free benzenediazoic acid has the nitroamine constitution,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NO}_2$ , but that it reacts as a tautomeric substance and can give rise to *O*- and *N*-derivatives:  $\text{C}_6\text{H}_5\cdot\text{NX}\cdot\text{NO}_2$  and  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NO}\cdot\text{OX}$ .

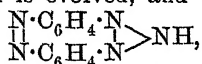
The ammonium salt of nitrosophenylhydroxylamine crystallises from alcohol in broad, silver-white needles, m. p.  $163-164^{\circ}$ , and sublimes on the water-bath in glistening plates. The iron salt separates from its light petroleum solution in the form of reddish-brown crystals, or from its ethereal solution in garnet-red needles with a blue, metallic lustre. The physical and chemical properties of the compound indicate that it is a complex metallic salt.

*p*-Chlorophenylnitrosohydroxylamine,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}(\text{NO})\cdot\text{OH}$ , is best separated from *p*-chlorobenzenediazoic acid (Abstr., 1897, i, 467) by conversion into its barium salt, which is insoluble in boiling water, and is then purified by conversion into the ferric compound. It crystallises from light petroleum, has m. p.  $73\cdot5-74\cdot5^{\circ}$ , and may also be prepared by the action of nitrous acid on *p*-chlorophenylhydroxylamine. The ammonium salt,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}(\text{NO})\cdot\text{ONH}_4$ , forms reddish-brown, glistening plates, m. p.  $164-165^{\circ}$ ; the phenylhydrazine salt forms colourless, glistening plates, m. p.  $115\cdot5-116\cdot5^{\circ}$ , and the hydroxylamine salt has m. p.  $93-96^{\circ}$  (decomp.). The iron compound forms dark red, glistening prisms.

*p*-Chlorophenylhydroxylamine,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{OH}$ , obtained from

*p*-chloronitrobenzene, crystallises from water in colourless, glistening plates, m. p. 86° J. J. S.

**Tri-imides of *m*- and *p*-Azo- and Azoxy-benzenes.** FRITZ BUCHNER (*J. pr. Chem.*, 1909, [ii], 80, 355—368.)—The author has prepared tri-imides of *m*- and *p*-azobenzene or azoxybenzene, analogous to the tri-imides or azoimides of the diphenyl series (Vaubel and Scheuer, *Abstr.*, 1906, i, 323), as follows. *m*:*m*'-Diaminoazobenzene is dissolved in glacial acetic acid, and treated with the requisite amount of hydrochloric acid and sodium nitrite; the resulting diazotised base is treated with ammonium hydroxide and heated, whereby nitrogen is evolved, and the *tri-imide*,



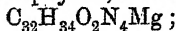
is produced. The *tri-imides* of *m*:*m*'-diaminoazoxybenzene and of *p*:*p*'-diaminoazobenzene have been prepared in the same way. None of the compounds are described. C. S.

**Protein-Cleavage by Dilute Mineral Acids.** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1909, 62, 492—495).—By boiling the iodo-protein prepared from egg-white with 10% sulphuric acid, the undissolved residue exhibits in different cases a widely varying percentage of iodine, whereas that of nitrogen varies within much narrower limits. The groups which combine with iodine are among others tyrosine and, perhaps, histidine. Similar results were obtained with iodothyreoglobulin. W. D. H.

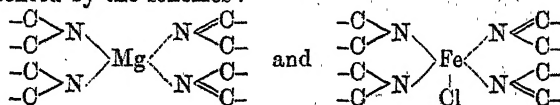
**Chemistry of the Bacterial Cellular Proteins.** SYBIL MAY WHEELER (*J. Biol. Chem.*, 1909, 6, 509—552).—These proteins were obtained in large quantities freed from non-toxic extractives soluble in alcohol and ether. They are highly poisonous whether prepared from pathogenic or non-pathogenic organisms. They give all the proteic colour tests; they are scarcely affected by physical solvents, but are partly digested by pepsin and trypsin with a lessening of their toxicity. Hydrolysis with mineral acids effects the usual cleavage, but does not separate the poisonous group in a free form. Hydrolysis with dilute alkali leaves the non-toxic portion undissolved; this is accompanied by loss of ammonia. The insoluble residue shows most of the proteic colour tests, contains all the carbohydrate and most of the phosphorus of the original, and is the specific part which immunises and sensitises. The poisonous portion is soluble in alcohol, and is lethal, and the symptoms are the same whatever protein is employed as its source. W. D.

**Linking of the Iron in the Colouring Matter of Blood.** RICHARD WILLSTÄTTER (*Ber.*, 1909, 42, 3985—).—In a forthcoming paper it will be shown that chlorophyll is from a tricarboxylic acid, and that on heating with concentrated

solution it yields, firstly, two dicarboxylic acids, glaucophyllin and rhodophyllin, containing magnesium, and then two monocarboxylic acids, pyrrophyllin and phyllophyllin, having the composition



these mono- and di-basic acids form salts and esters, their carboxyl groups not being related to the metal present in the complexes (compare Willstätter and Pfannenstiel, Abstr., 1908, i, 198). The magnesium in chlorophyll and the group FeCl in hæmoglobin are similarly combined, rhodophyllin and hæmin being analogous dicarboxylic acids (compare Nencki and Zaleski, Abstr., 1900, i, 709; Zaleski, Abstr., 1903, i, 217). Piloty and Merzbacher's conclusion (this vol., i, 857) that the iron atom in hæmin and in hæmatin is united with the two carboxyl groups is inadmissible, since hæmin is not the iron salt of a carboxylic acid, but a free acid. The conclusion must be drawn that the metal in chlorophyll and in hæmin is united only to nitrogen, and in accord with Ley and Werner's views concerning the constitution of complex metallic salts of acid imides, biuret and dicyanodiamidine (Abstr., 1907, i, 302; see also Tschugaeff, *ibid.*, 595), the author regards the condition in which the magnesium atom exists in the chlorophyll molecule and the group FeCl in the hæmin molecule as represented by the schemes:



T. H. P.

**The Destructive Effects of Shaking on Proteolytic Enzymes.** A. O. SHAKLEE and SAMUEL J. MELTZER (*Amer. J. Physiol.*, 1909, 25, 81—112. Compare this vol., i, 277; Harlow and Stiles, this vol., i, 861). Shaking in time destroys pepsin, rennin, and trypsin, specially readily at high temperatures; trypsin is more readily destroyed than pepsin. The assumption is made that what occurs is similar to the destruction of living cells, both these and enzymes living to some extent a similar structure.

W. D. H.

**m-Nitro-p-aminophenylarsinic Acid.** EFISIO MAMELI (*Boll. m. Farm.*, 1909, 48, 682—683).—*m*-Nitro-p-aminophenylarsinic acid,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{AsO}(\text{OH})_2$ , obtained by the interaction of arsenic in and *o*-nitroaniline, separates from water as a microcrystalline pure, behaves as a dibasic acid towards phenolphthalein, and yields light-yellow nitroaniline when its sodium salt is treated with potassium permanganate and sulphuric acid. The sodium, ammonium, silver, barium, ammonium, and copper salts are all stable.

*m*-Nitro-p-aminophenylarsenic iodide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{AsI}_2$ , prepared by the action of concentrated hydriodic acid on the preceding compound, m. p. 96°.

T. H. P.

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